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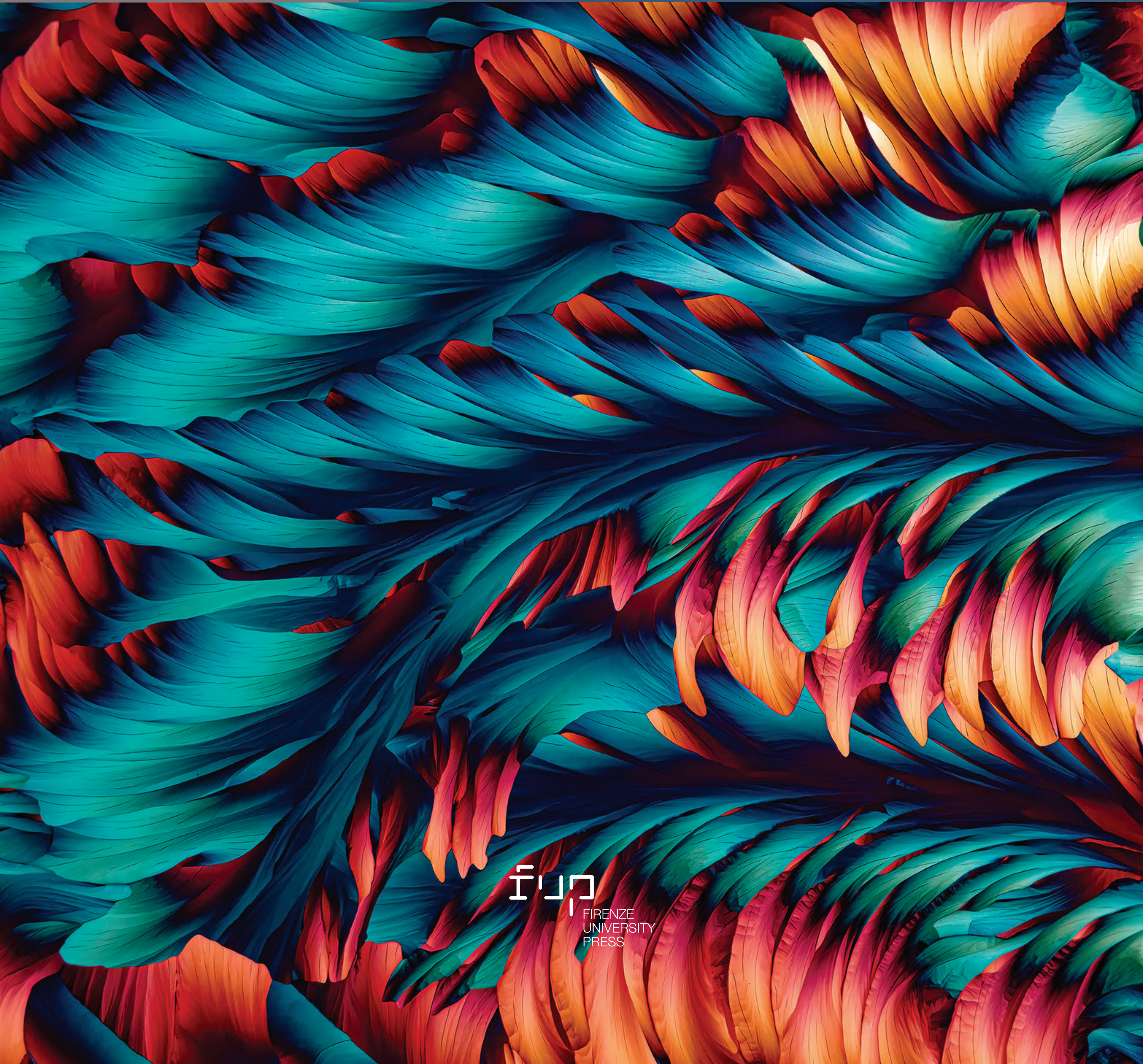

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Editorial

Why Basic Science Must Remain Free

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Across evaluation panels for funding and job positions and strategic research agendas a clear pattern has emerged: scientific research is increasingly expected to justify itself through immediate applicability. Grant calls emphasize industrial partnerships, technological transfer, measurable impact, and short-term deliverables. Proposals are routinely evaluated and selected not only for their intellectual value but largely for their potential to generate marketable products, policy instruments, or societal solutions within tight timeframes.

The emphasis on applicability is comprehensible but on its own it cannot justify the current trend. Public investment in research is substantial, and accountability is legitimate. Mankind is facing urgent challenges, including hunger, water supplies, climate changes, energy transition, public health crises, food security, wars and geopolitical conflicts, that demand scientific engagement. Needless to say, these problems tragically affect the life of poor people and of developing countries, while rich nations are less affected or can afford some concrete actions to mitigate their effects. Yet, in the rush toward utility a fundamental principle risks a serious danger: the protection of basic science conducted without predefined practical constraints.

Basic science—driven by curiosity rather than by immediate use—is the foundation upon which applied innovation ultimately rests. It is neither an extravagance nor an academic gratification. Instead, it is the generative substrate of any discovery. History repeatedly demonstrates that the most consequential applications often arise from investigations that were not conceived with application in mind.

Quantum mechanics was not developed to enable semiconductors. Number theory was not formalized to secure digital communication. Studies of bacterial adaptive immunity were not designed to produce CRISPR gene editing technologies [1]. In each case, conceptual investigation preceded application—often by decades. In other cases, it was technology that preceded basic science and urged for new theoretical formulations.

The problem with requiring predefined applicability is not simply that it biases funding allocations. It reshapes the culture of science itself. Somehow in our times science and scientists are looking for the approval of the public, as in a TV show. Today everything is measured in terms of performance and efficacy. Science and more in general culture are subject to a generic consensus, that for a politician means more votes (with the exception of autocracies that are pretty popular in these times).

When researchers internalize the expectation that projects must align with industrial or commercial demand, several distortions may emerge. Usually projects become more and more conservative, focusing on topics that will provide "useful" and certain results in a not-too-long period of time. Second, politically and economically interesting topics will be promoted and financed, while less visible or less exploitable research will be sacrificed. Third, in general the evaluation takes into consideration the production of deliverables and a timeframe of about 3 to 5 years. Finally, proposals that are not rooted on solid and (apparently) well established theories are discarded as non-repayable.

For all these reasons there is a real risk of weakening the intellectual biodiversity of science, that is the real and fundamental fuel for the advancement of knowledge. Basic science generates frameworks, methods, and theoretical architectures that may later prove indispensable in unforeseen contexts.

The value chain of knowledge is non-linear. Breakthroughs frequently arise at disciplinary margins, in

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exploratory work unconstrained by immediate demand. To suppress such exploration is to diminish the probability space of future innovation. Remember the lesson from James Clerk Maxwell on “crossed fertilization” among different disciplines [2], to be extended to basic science and applications.

Another despicable effect of this way of doing science has to do with the younger generations of scientists. Early-career researchers are increasingly trained in environments where grant-writing emphasizes impact narratives over intellectual audacity. If funding structures consistently privilege applied framing, young scientists may never be able to experience the search for fundamentals, especially those that are more challenging and still unresolved.

Of course, basic science is not opposed to applied research. On the contrary, both are necessary and mutually reinforcing. But applicability and performance cannot be taken as stringent criteria to recognize and support important research themes. People need answer for several concrete and practical issues but other sources of funding need to nourish fundamental research without the demand for rapid and efficient solutions. In fact citizens benefit not only from new devices and innovative therapies, but also from the deepening of knowledge. People must be persuaded that this is reasonable and sustainable.

Some guidelines for a correct adjustment between these two tracks should include: (1) Appropriate funding sources finalized to support proposals that address fundamental topics with a high level of intellectual originality and methodological rigor. (2) A longer timeframe for such theoretical or exploratory work where it is unforeseeable the production of deliverables in short times, with the understanding and recognition that conceptual advances represent a strong impacting result as they prompt (in due time) and stimulate applied research with all its outcomes.

In times of economic difficulties or when political elections approach, politicians become more sensitive to these issues and the temptation to concentrate on visible outputs is real. However without the advancement of basic science, applied research eventually exhausts its substrate and will not be able to face the new challenges.

The protection and promotion of basic science is not for nostalgic aficionados of an idealized old style academic past. But rather it is a farseeing investment in science, culture, education and pratical outcomes. The discoveries that will address the grand challenges of the coming decades may already be incubating in laboratories and theoretical explorations that, at present, appear detached from immediate utility.

The responsibility of research institutions, funding bodies, and scholarly communities is to ensure that such incubators are not extinguished by a narrow and anti-scientific conception of relevance.

When I was a teenager, politicians belonging to all parties used to explain people their short- and long-term policies, including the scientific and technological progress of the society. And certainly there was a respectful attitude toward science and scientists. Regretfully we have to recognize that this powerful and sensible push is dismissed todays and politics is driven by polls, not by a wise and shared perspective in pursuing the common good. Fifty years ago these words meant something, today they would be misunderstood if not discarded as ridiculous.

NOTES AND REFERENCES

[1] Clustered Regularly Interspaced Short Palindromic Repeats, a revolutionary gene-editing technology derived from a natural defense mechanism in bacteria. It acts as a precise, fast, and economical molecular tool to modify, delete, or regulate DNA sequences in living organisms.

[2] J.S. Reid, C.H.-T Wang, J.M.T. Thompson. “James Clerk Maxwell 150 years on”. *Philos Trans A Math Phys Eng Sci* **2008**, *366*, 1651–1659. DOI: 10.1098/rsta.2007.2196.

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Research Article

Electrophotonic Analysis (EPA) of Tap Water Droplets Versus Hydro-Alcoholic Solutions

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Abstract. Aim: The lack of precision of validated electrochemical identification methods and the limited detection of compounds at low concentrations by spectrometric methods are well known. Physics has provided a strong theoretical background, and modern technologies allow the development of electro photonic analytical devices that aim to provide greater precision in the detection of compounds, even at low concentrations. This original article provides a new experimental and theoretical insight into chemistry. Method: This paper describes the theory and the technical aspects of the electro photonic analysis method. This technology is tested on samples of tap water droplets compared to hydro-alcoholic solutions (ethanol 62% m/m). Results: Using repeated measurements on the same tap water and ethanolic solutions, we demonstrate the reproducibility of the method. This method can now be systematically double-blind tested on a variety of samples.

Keywords: Electrophotonic analysis, Corona discharge, Validation, Reproducibility, Discriminatory potential, Photon electrochemistry.

INTRODUCTION

Water is a complex substance characterized by thermodynamic coefficients displaying a highly non-linear change with temperature or pressure [1]. One of the most amazing properties of liquid water is its ability to reduce its volume upon heating between 0°C and 4°C. Galileo already discussed such an anomaly about four hundred years ago [2]. Water is also an essential element for life and for many religious beliefs [3]. Among all known substances, water displays the highest ratio of Boyle's temperature to molecular weight [4]. Moreover, considering cosmic abundances of the elements in the universe one gets the following order: hydrogen > helium > oxygen [5]. Consequently, as helium is an unreactive gas, water is also the most abundant substance of the universe. To best realize the strangeness of water, one may rely on the fact that upon heating, molecules should acquire more kinetic energy, allowing them to increase the volume holding them together. This is not the case with liquid water where more thermal energy below 4°C leads to a reduction in volume. It is not an easy matter for science to explain such an amazing fact. In fact, only quantum physics deal easily with such a phenomenon [6, 7]. Basically, the anomaly comes from the formation of coherence domains that also explains why water, a diamagnetic substance, is strongly affected by magnetic fields [8]. This has the amazing consequence of being able to synthesize a DNA-molecule from scratch using electromagnetic information [9,10]. Hydrogen bonding plays a key role in corona discharges in water by influencing cohesion and the stability of hydrated electrons, which are formed and react via hydrogen bonds during the process [11,12]. Another sequel is that water is expected to play a crucial role in the manifestation of consciousness in living beings [13]. The fact that liquid water may acquire a nanostructure (coherence domains) by coupling with the fluctuating electromagnetic fields filling the quantum vacuum helps understanding, for instance, how high dilutions may have a biological effect despite the absence of any solute species [14,15].

However, as coherence concerns quantum phases that are not physically observable, conventional physicochemical measurements are of very limited use. There is a need to use non-conventional techniques, for characterization of the information stored in these putative coherence domains. Among such techniques, we may cite electrochemical impedance spectroscopy (EIS) [16], aqua-photomics [17], evaporated water droplets patterns [18] or sensitive crystallization [19]. Alternatively, one may use lyophilization techniques to recover solid residues analyzed by more conventional techniques [20]. Herein, we have applied a technique, named electrophotonic analysis (EPA) based on Corona discharges [21-24]. This technique is well adapted for studying solids or liquids. It has proven to be very sensitive, producing images that can be quantitatively analyzed using classical procedures in medical imaging.

2. BACKGROUND

Corona discharges also known as St. Elmo's fires are well-documented natural phenomena that were already known in ancient Greece. About sixty years ago, a corona-based technique named "Kirlian photography" was developed in Russia [25]. The idea was to record a photographic image of an object after applying a large electric potential between the object and a dielectrically isolated electrode. As such a technique, called corona discharge photography (CDP) may be applied to human subjects, it has rapidly been claimed that variations in image structure can be related to changes in physiological, psychological and psychic states [26]. Further studies have revealed that upon application of a high voltage (15-60 kV) to matter, a few electrons are first produced between the object and the isolated electrode. Further acceleration of these electrons by the electrical field provokes ionization of the surrounding gas (generally air). This leads to an exponential growth in the number of electrons and positive counter-ions. The electrons sweep quickly toward the positive anode, while the cluster of positive ions moves somewhat more slowly toward the negative cathode. When the positive ion cluster in the air gap reached a critical density, many recombination events with electrons occur. Such events lead to a large emission of light photons in the UV-region of the electromagnetic spectrum having also a tail in the visible region (bright blue color). The cluster of positive ions then becomes brightly illuminated with both positive and negative streamers between the electrodes. Consequently, discrete balls of light move in various directions.

Rigorous experiments have shown that charge recombination processes create streamer images extending radially from the sample- electrode boundary [27]. It was observed that for a given voltage pulse and pulse repetition rate, the streamer range is dependent on the electric field bending due to the mismatch of dielectric constants et dielectric interfaces, the relative thickness of the dielectric components between the sample and the voltage source, the water vapor content of the atmosphere and the geometric characteristics of sample's surface.

More particularly, this range is proportional to the corona onset voltage. It is an inverse function of the resistance formed by the high-voltage anode and the sample. For a given resistance, water vapor reduces streamer range by absorbing photons which otherwise would be available for propagating positive streamers by photoionization. Water vapor may also reduce streamer breakdown voltage by influencing the charge sheath that forms above a positive point.

The absence of streamers within a given region of the sample-electrode boundary is predominantly due to the release of water present on or within the sample.

The existence of corona streamers that deviate significantly from a radial trajectory is another phenomenon that is related to moisture. Accordingly, streamers that have curved paths usually outline regions in which streamers are absent, and frequently curve into these empty regions, electrons being attracted there by a positive density of charges sustained by water molecules.

Consequently, streamer curvature is not observed when the samples are dry. It follows that most of the variations in the images of corona of a sample in contact with the anode may be accounted for by the presence of moisture on or within the sample's surface. During exposure, moisture is transferred from the sample to the anode and causes an alteration of the electric charge pattern on the anode, hence the electric field at the surface of the sample. As a result, large variations in the density of corona images as well as corona streamer range and trajectories may be brought about.

For biological substances, it has been confirmed that light emission mirrors the moisture content and geometry of the object [28]. In the case of living tissues, no evidence was related to the activity of either plant or animal cells. No evidence of any property of the corona pattern could be related to the physiological, psychological or psychic condition of the samples [29]. It was also concluded that CDP could contribute to those areas in science where conductivity and surface arrangement of the conducting areas play a major role [30]. More recent studies have however concluded that there was mounting evidence that CDP diagnosis for living tissues has an important part to play within both orthodox and complementary therapies in medicine [31]. More research is thus needed on this technique that could lead to very complex images.

It was also shown that photographic material was not necessary for recording halo, streamers and other details typical of CDP photographs [32]. Such images may then be recorded on any bulk dielectrics and on thin films of various materials deposited on glass substrates. A significant advance in this field was the possibility of using modern optics; electronics and computer processing leading to the so-called gas discharge electro photon capture (EPC) analysis based on gas discharge visualization (GDV) technique [33]. It has then been claimed that EPC can be implemented as an express method for assessment of treatment procedures effectiveness, evaluating emotional and physical conditions of people [33]. The technique seems to be sensitive enough to detect temperature, air humidity, air pressure, gender, age, heartbeat, and blood pressure effects on recorded images after a short contact with various textiles [34]. Another interesting aspect of the technique is the possibility of detecting weak transformation of water under the influence of electromagnetic fields, air, light and other subtle factors [35]. Finally, the EPC/GDV technique has also previously been used for investigating the concentration dependence of corona discharges around drops of inorganic electrolytes [36].

The motivation of this study was then to check if electrophonic analysis (EPA) could be a valuable scientific tool for differentiating among various kinds of liquid water samples, mixed or not with alcohol. The spirit was to use a highly sophisticated device developed by the company CORAMP solutions based in Brens (France) and to use a large set of image analysis techniques for retrieving information embedded in EPA images. As any piece of matter contains a variable amount of water, it follows that corona discharge imaging may be very useful in the detection and quantification of moisture or others compounds in animate or inanimate specimens through the orderly modulation of the image due to various levels of these compounds. It was further hoped that differences observed in corona images might also reflect a change in liquid as well as interfacial water.

3. METHODS

3.1 Experimental setup

Our measuring device (figure 1) is based on a Advanced Electro Photonic Generator (AEPG©). It is able producing a stable and reproducible electromagnetic field both in voltage and frequency. This generator, coupled with other components controlled by highly reliable electronics, produces with its strong pulse voltage, an electromagnetic field on the electrode plate. This field is alternately positive and negative, with a predefined frequency. This field successively mobilizes electric charges at the surface and in the thickness of the object to be analyzed causing ionization of the gaseous environment around the studied body (plasma gas). This ionization creates an electronic avalanche, which by splitting the gas molecules, release UV photons that are recorded by the Hamamatsu camera. All these phenomena don't appear simultaneously, but one after the other, depending on the pulse generator. Images acquisition provides an idea of the statistical distribution of light emission during exposure time. Numerous experiments have shown that charges are mainly distributed in two different ways:

– The positive pulses of the generator, leading to filamentary structures called “streamers”.

– The negative pulses creating rounded and globular forms called “coronae”.

These acquisitions enable an appreciation of the increasing richness of the image as the complexity of the analyzed object grows.

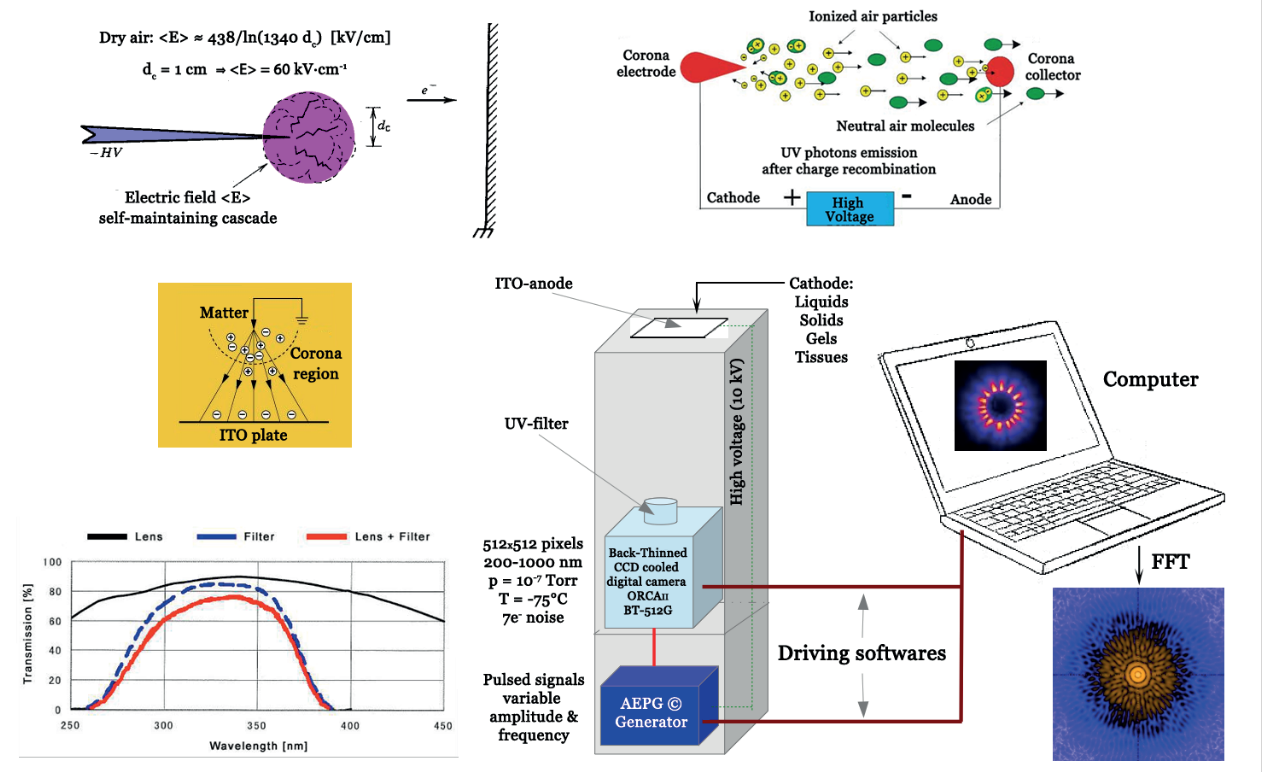


Figure 1: *Principles of the corona effect and experimental device for recording electrophotonic images.*

To this generator is attached an EFUSE© a transparent and conductive electrode plate having the highest possible homogeneity at each point of its surface allowing good control of the distribution of electrical charges. For recording the photonic emission, we have used a Hamamatsu HD camera (ORCA IIBT 512G2) with a specific timing and adjustable exposure time coupled to an optical equipped with a UV filter.

It is worth noticing that many environmental physical factors are to be taken into account in conducting electrophotonic experiments. Among them, we may cite: ambient atmosphere (gas), moisture (crucial factor for ionization), and dust (highly sensitive to electric fields). Table 1 gives the recorded experimental conditions concerning acquisition of the images.

Table 1: *Conditions in the laboratory during acquisition of electrophotonic images.*

Parameter	Value
T(inside) /°C	19
T(outside) /°C	20
R.H. %	78
Voltage / kV	11
Frequency / Hz	110
Weather	sunny

Figure 2 shows the experimental setup used for recording images on water droplets.

A total of 12 images have been captured of Brens' tap water droplets. The measures were implemented in September 2019. The aim was to establish whether it was possible to obtain reproducible images of identical droplets using a technique that is renowned for being highly sensitive to environmental factors. Minerals in used tap water are: Calcium: 88.7 mg/L; Potassium: 0.9 mg/L; Magnesium: 9.8 mg/L; Sodium: 3.2 mg/L; Sulphates: 8.9 mg/L.

Other measurements were carried out as part of a test of the technique in March 2016 (comparable experimental parameters). Three images of a concentrated mother tincture of Gelsemium were compared to three images of the same ethanol/water percentages without plant extract (appropriate control). The aim was to establish whether this method could distinguish between these preparations. These measurements were taken in a double-blind manner, meaning that the researcher did not know which sample was being analyzed.

Another 12 images correspond to strongly diluted (above the Avogadro number) plant extract (Gelsemium) in a mix of ethanol/deionized water (62% m/m of ethanol) were finally compared to the tap water results. The aim was to extend the comparison between tap water and the alcohol/water mixture.

These measures are preliminary and are intended solely to verify the method's validity and its potential for further development. The characterization of other liquid water samples (mineral water, seawater, contaminated water, water subjected to vortex or electromagnetic fields, homeopathic remedies, etc.) could be reported in future papers. Different percentages alcohol/water mix could also be measured. The choice of 62% m/m ethanol concentration is necessary as an appropriate control for Gelsemium mother tincture.

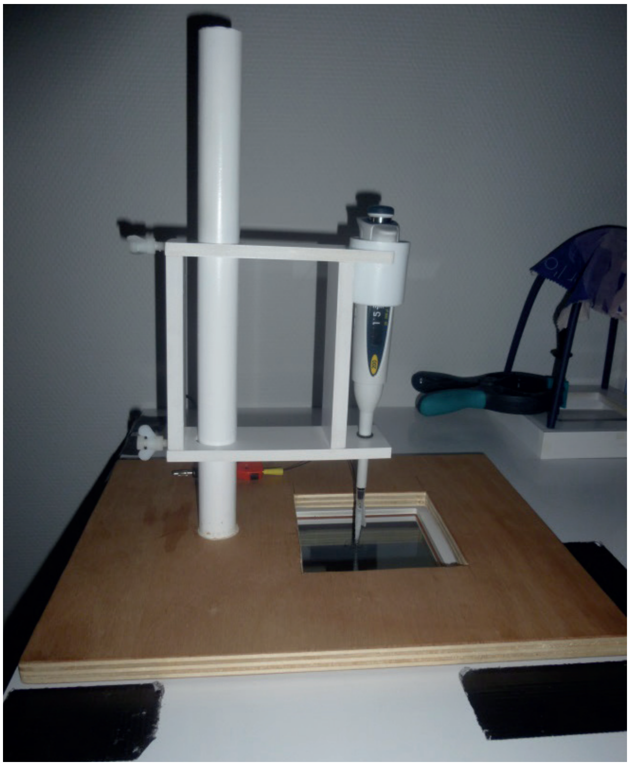


Figure 2: *Experimental setting for recording electrophotonic images on water or liquid droplets.*

The volume of the analyzed droplet is maximized as closely as possible to the moment it falls from the pipette. Ideally, for a new prototype, a computer would determine this volume, and an automated pipette would perform pipetting to avoid possible small volume variations.

Other experimental parameters in 2016: Millipore RX 45 series water apparatus, serial number FSDM 96292D; Ethanol 96%V/V Ph.Eur. in 1-liter bottles Certa. Batch 15H20-C01-16756 P.23 09 2015 Exp. 08 2018. Verg.nr.597R01872 UN1170; 500 ml bottle of Gelsemium Sempervirens HAB Heel mother tincture, supplied by Homeoden in a PET bottle. Batch 548463. Expiry date: 12/2018/ 982 UH 911F34

To extend the measurements to other types of solution, we plan to use AI. This will require us to multiply the number of measurements several hundredfold in order to generate a database of reference images.

Several strategies are available for computer analysis of EPA images, free of subjective estimation. The first strategy is to determine the center of the investigated object followed by the determination of its border. Then, one could study the angular dependence of luminosity with a fixed resolution of a few degrees. From angular dependence, the streamers that are more or less prominent radial ray-like formations, are determined and their characteristics (height, width, etc.) calculated. Using this technique, it was possible to evidence distinct behavior of corona discharges patterns as regards ionic composition of salts in water, both radially and angularly [37]. If such a method seems well adapted for drops of solutions, it cannot be used for solids where streamers are systematically very short and very thin and hardly discernable from a more or less globular halo. New strategies have thus been developed for automatic analysis of EPA images. The strategy is a detailed analysis of the shapes that may be recognized in the pictures and analyzed in terms of geometric parameters. A second strategy is to perform the same kind of tasks on a spatial Fourier transform of the images.

3.2 Image processing 3.3 Contrast enhancement 3.4 Color enhancement 3.5 Thresholding algorithms 3.6 Geometrical analysis (See Supplementary material)

3.7 Measured parameters

The measurements are repeated on different well-defined areas of the colored and FFT images obtained. 2 areas for the colored versions, 5 areas for the FFT views. Figure 3 is an example of the development of one of these images. Figure 4 allows us to compare 3 source images of pure ethanol 62% m/m and of the mother tincture of a plant Gelsemium sempervirens containing also ethanol 62% m/m.

3.8 Normalization of data

Data normalization aims to transform the values of the dataset into the same scale [92-94]. For multiple data sets where variability is justified by measurements that can be influenced by technical or environmental factors, standardization on one parameter is appropriate. For EPA, the internal areas analyzed must be comparable in size.

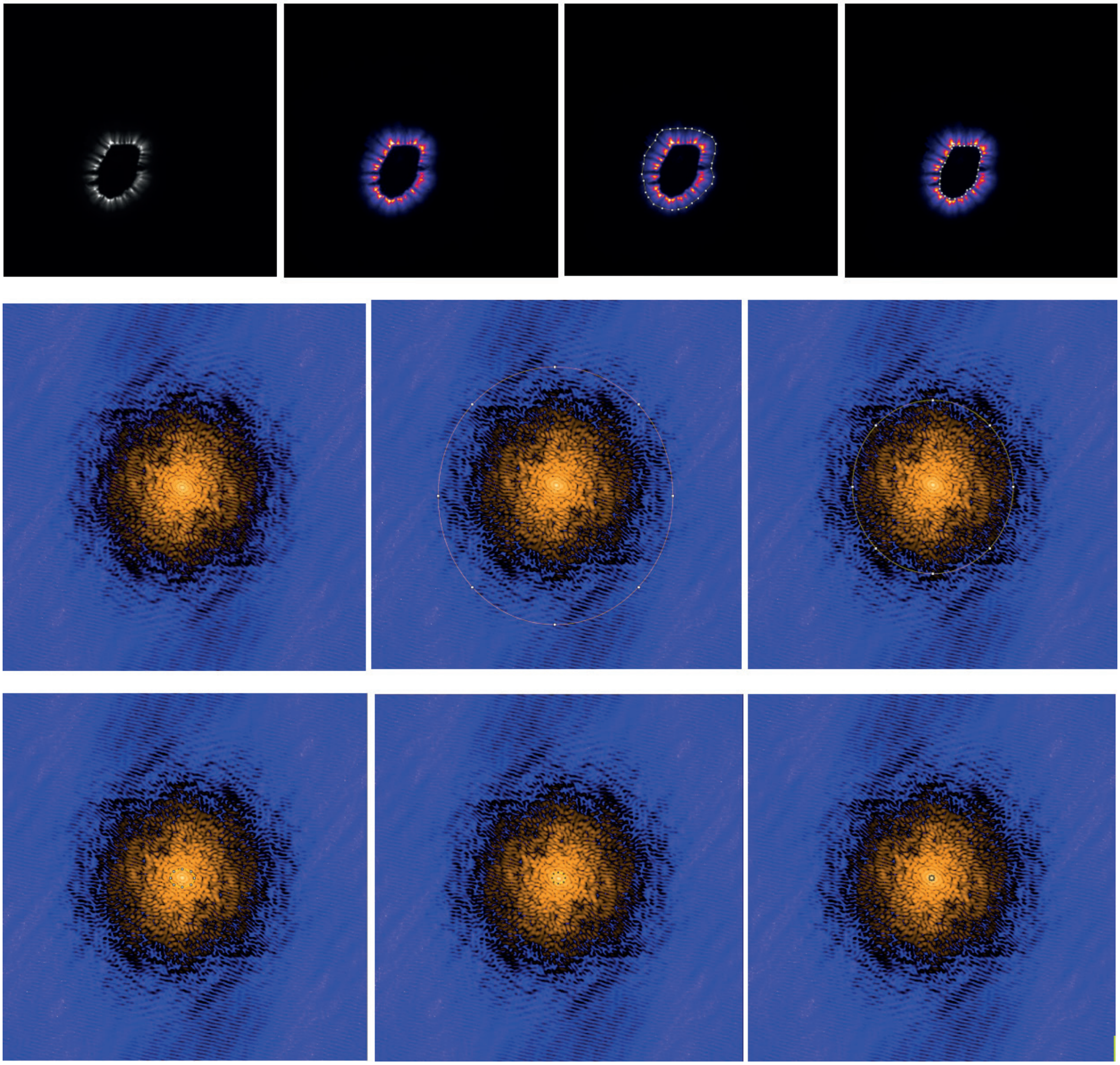


Figure 3: *Black and white, colored and FFT image and the selected surfaces on a water droplet (external selection, brightest selection, center 1, 2 and 3).*

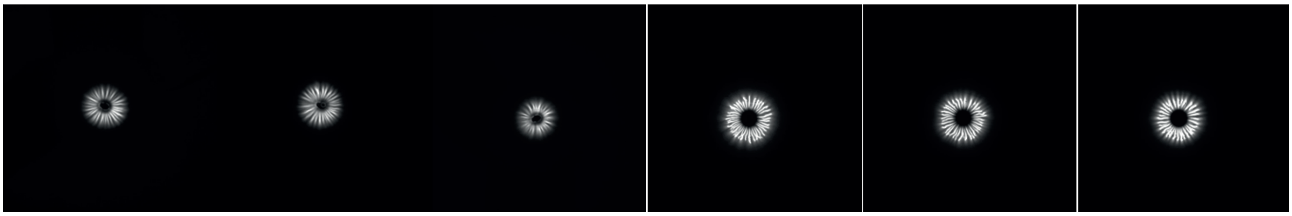


Figure 4: *Source images of ethanolic solutions. The 3 on the left are the pure hydroalcoholic solution, on the right the 3 images of the mother tincture of the plant Gelsemium. Both solutions contain 62% m/m of ethanol.*

3.9 Statistical analysis

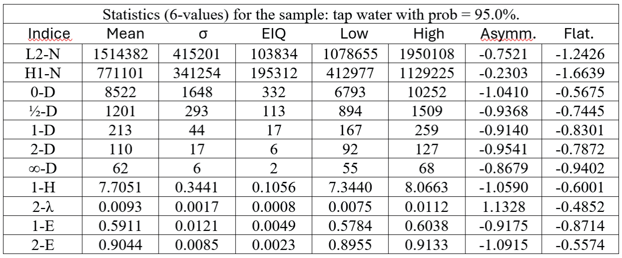
All statistical analyses were performed on EPA raw data using SigmaStat version 4, a wizard-based statistical software package designed to guide users through each step of the procedure. For multiple comparisons, two- or three-way analyses of variance (ANOVAs) were applied after the normality (Shapiro–Wilk test) and equality of variances (Brown–Forsythe test) were validated. The following specific pairwise multiple comparison procedures were suggested: The Tukey test for two-way ANOVA and the Holm-Sidak method for three-way ANOVA. The significance level was set at 0.05.

4. RESULTS

One of the main advantages of recording EPA images is the extreme sensitivity of the technique. It may then be anticipated that small changes around the droplet, atmosphere's temperature as well as relative humidity or electromagnetic background could lead to completely different images for the same sample. To check further this point, twelve images have been captured for tap water.

As a preliminary step, six images were analyzed using the Weber algorithm and five local adaptive thresholding techniques (Bernsen, Niblack, Sauvola, Phansalkar, and Savakis). Reproducibility at the 95% level was observed for all these parameters (Table 2) between these six images.

Table 2: *Results of statistical analysis using five local adaptive thresholding techniques for parameters of the 6 first tap water photographs.*



Statistics (6-values) for the sample: tap water with prob = 95.0%.							
Indice	Mean	σ	EIQ	Low	High	Asymm.	Flat.
L2-N	1514382	415201	103834	1078655	1950108	-0.7521	-1.2426
H1-N	771101	341254	195312	412977	1129225	-0.2303	-1.6639
0-D	8522	1648	332	6793	10252	-1.0410	-0.5675
½-D	1201	293	113	894	1509	-0.9368	-0.7445
1-D	213	44	17	167	259	-0.9140	-0.8301
2-D	110	17	6	92	127	-0.9541	-0.7872
∞-D	62	6	2	55	68	-0.8679	-0.9402
1-H	7.7051	0.3441	0.1056	7.3440	8.0663	-1.0590	-0.6001
2-λ	0.0093	0.0017	0.0008	0.0075	0.0112	1.1328	-0.4852
1-E	0.5911	0.0121	0.0049	0.5784	0.6038	-0.9175	-0.8714
2-E	0.9044	0.0085	0.0023	0.8955	0.9133	-1.0915	-0.5574

The analysis described in section 3.7 has been applied to a second set of 12 analyzed images to check reproducibility once more.

A/ In terms of the global image (without area selection), the area geometry parameters are always the same. Table 3 shows the coefficients of variability for the other parameters of 12 tap water source photographs. Table 4 shows these variances for the 7 selected areas (2 colored and 5 FFT images see Fig 3).

Table 3: *Coefficients of variability looking at the images without any area selection (global image) for parameters of the 12 tap water photographs.*

Measured parameters	Global Black & White	Global coloured	Global FFT
Mean	2%	7%	13%
StdDev	6%	4%	3%
Mode	0%	4%	26%
Min	0,7%	0%	0%
Max	0%	2%	1%
XM	0,6%	2%	0%
YM	1%	3%	0%
Median	0,3%	3%	16%
Skew	6%	6%	62%
Kurt	12%	17%	>100%

Table 4: *Coefficients of variability between parameters of the 12 tap water source photographs calculated for the selected areas.*

Measured parameters	Color External selection	Color Internal selection	FFT External selection	FFT Brightest Selection	FFT Center 3	FFT Center 2	FFT Center 1
Area	6%	8%	19%	16%	26%	12%	32%
Mean	8%	5%	3%	2%	2%	1%	1%
StdDev	8%	3%	3%	3%	10%	11%	12%
Mode	7%	4%	3%	2%	2%	4%	3%
Min	3%	2%	4%	22%	10%	6%	5%
Max	0%	3%	0%	0%	0%	0%	0%
X	2%	2%	1%	1%	0,1%	0,2%	0,1%
Y	3%	3%	2%	0 ,7%	0,2%	0,1%	0,2%
XM	3%	2%	1%	0 ,9%	0,1%	0,2%	0,1%
YM	3%	3%	1%	0,6%	0,1%	0,1%	0,2%
Perim	3%	6%	9%	8%	12%	5%	15%
BX	3%	3%	21%	7%	0,9%	0,2%	0,3%
BY	5%	5%	22%	9%	0,8%	0,2%	0,3%
Width	3%	6%	10%	8%	13%	6%	16%
Height	5%	9%	10%	10%	12%	8%	16%
Major	5%	8%	9%	9%	13%	5%	17%
Minor	4%	6%	9%	8%	12%	8%	16%
Angle	3%	28%	73%	88%	0%	>100%	>100%
Circ	3%	6%	2%	5%	0,9%	0,4%	1%
Feret	5%	8%	9%	9%	13%	0,5%	17%
Median	14%	3%	3%	3%	0,1%	0,1%	2%
Skew	12%	15%	24%	35%	99%	64%	>100%
Kurt	23%	36%	66%	57%	57%	77%	61%
FeretX	10%	4%	46%	32%	0,9%	0,1%	0,4%
FeretY	24%	17%	24%	20%	0,2%	0,1%	0,4%
FeretAngle	40%	34%	73%	88%	0%	>100%	>100%
Min Feret	3%	8%	9%	8%	12%	8%	14%
AR	6%	12%	4%	6%	0,8%	7%	11%
Round	6%	12%	4%	5%	0,7%	6%	10%
Solidity	1%	3%	0%	0%	0,9%	2%	8%

B/ To test the potential of the method to discriminate between two images, we compared first, 3 images of pure ethanolic solution and 3 of a concentrated mother tincture. Both are titrated to 62% m/m ethanol (figure 4).

Analyzing these 6 images, only 2 of the 30 parameters related to the vertical axis of the image (Y, YM) did not pass the 3-way ANOVA test. This statistical approach allows us to check the ability to discriminate between two different products, but also between the selected areas. It also provides another way of checking the reproducibility of the method. Normality test passed everywhere except for Mode and FeretX. Variance passed everywhere. Discrimination between ethanol and mother tincture (product) was successful for 20 parameters for the outer perimeter selection and for 18 parameters for the central dark area. Failures are expected because, in these hydroalcoholic images the shape is perfectly round, in which case the angular parameters cannot be used for differentiation.

Table 5: *Statistical analysis of the indexes measured on the electrophotonic images. Highlighted in pink are results statistically significant (p=<0.05) in favor of discrimination.*

Measured parameters	Ethanol		Gelsemium		ANOVA-3w	Normality	Variance	P-value between		
	Mean	StdDev	Mean	StdDev				Product (n=2)	Zone (n=2)	Sample (n=3)
Area	4875	4152	11173	10784	OK	Passed	Passed	0,034	<0.001	0,845
Mean	81824	17709	51227	38175	OK	Passed	Passed	0,006	<0,001	0,919
StdDev	46983	9037	45339	34092	OK	Passed	Passed	0,862	0,004	0,958
Mode	26	17	132	135	OK	Failed	Passed	0,037	0,013	0,991
Min	8	1	6	1	OK	Passed	Passed	<0.001	1,000	<0.001
Max	224	38	177	86	OK	Passed	Passed	0,046	<0.001	0,784
X	247	3	241	1	OK	Passed	Passed	<0.001	0,190	0,238
Y	272	2	273	1	NS	Passed	Passed	0,264	0,787	0,583
XM	247	3	240	1	OK	Passed	Passed	<0.001	0,877	0,355
YM	271	2	273	1	NS	Passed	Passed	0,094	0,578	0,738
Perim.	224	116	324	206	OK	Passed	Passed	0,019	<0.001	0,869
BX	211	20	189	34	OK	Passed	Passed	0,005	<0.001	0,733
BY	237	19	222	32	OK	Passed	Passed	0,022	<0.001	0,791
Width	72	36	104	66	OK	Passed	Passed	0,023	<0.001	0,897
Height	71	37	103	65	OK	Passed	Passed	0,016	<0.001	0,836
Major	72	37	104	66	OK	Passed	Passed	0,020	<0.001	0,899
Minor	70	37	102	65	OK	Passed	Passed	0,018	<0.001	0,836
Angle	15	37	45	49	NS	Passed	Passed	0,334	1,000	0,772
Circ.	0,998	0,003	1,000	0,000	NS	Passed	Passed	0,130	0,203	0,358
Feret	72	37	104	66	OK	Passed	Passed	0,020	<0.001	0,897
Median	74	15	34	28	OK	Passed	Passed	<0.001	<0.001	0,779
Skew	0,584	0,122	1,623	0,656	OK	Passed	Passed	0,006	0,096	0,993
Kurt	-0,361	0,199	2,397	2,760	OK	Failed	Passed	0,027	0,045	0,993
FeretX	219	20	209	42	NS	Passed	Passed	0,578	0,107	0,703
FeretY	281	22	293	30	NS	Passed	Passed	0,481	0,406	0,722
FeretAngle	15	37	45	49	NS	Passed	Passed	0,334	1,000	0,772
MinFeret	70	37	102	65	OK	Passed	Passed	0,018	<0.001	0,837
AR	1,036	0,038	1,028	0,024	OK	Passed	Passed	0,531	0,031	0,093
Round	0,967	0,034	0,974	0,022	OK	Passed	Passed	0,553	0,027	0,096
Solidity	0,996	0,002	1,003	0,006	OK	Passed	Passed	0,038	0,563	0,711

About the reproducibility of the measurements between the 3 samples of the same product, the difference in the mean values between them is not so great as to exclude the possibility that the little differences are simply due to random sampling variability (Table 5 - Figure 5).

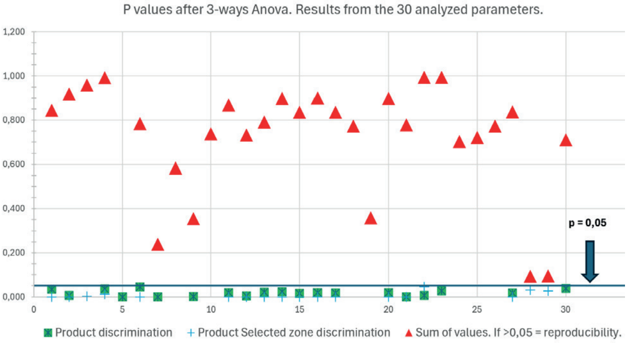


Figure 5: *Statistical analysis of the parameters measured on the electrophotonic images.*

The same analysis can be done on the selected areas of the FFT images (Fig 3). However, we can see that the outermost central zone 3, which is clearly visible in the Gelsemium mother tincture image, is missing from the ethanol FFT images (Fig 6). The 3 ethanol images have only 2 concentric circles, hexagonal in the middle, whereas the images of the tincture of Gelsemium, like the tap water drops above, have a third additional circle around the center. This discrimination is possible because a specific luminous wavelength is expressed for Gelsemium, but not for ethanol. For the remaining 4 selected shared areas the 3-way ANOVA procedure has been followed for the 30 parameters, aiming to assess the potential for discrimination between these two products. Analyses of the other areas did not enable them to distinguish between the wavelengths of light emitted by ethanol control and the Gelsemium mother tincture.

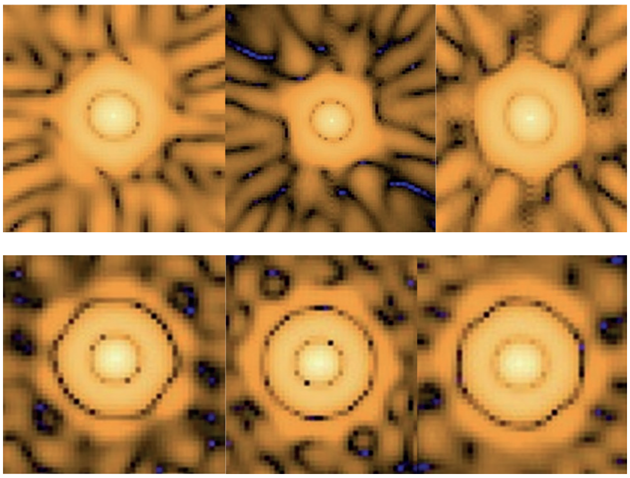


Figure 6: *The central areas of the three images of 62% ethanol are shown above. The three images of the Gelsemium mother tincture, which also has a 62% alcohol content, are shown below.*

C/ The third stage of this validation is to compare the above mentioned 12 images of drops of tap water with 12 images of Gelsemium (62%m/m), at very high dilutions. The solvent used for these dilutions is an alcohol/water mixture titrated to 62% m/m ethanol. These images were taken randomly over 4 consecutive days (Figure 7). Small natural variations in temperature and humidity at the sites must be considered.

The differences between tap water and hydroalcoholic solutions of Gelsemium are obvious (Fig 7). Streams are longer for Gelsemium, dark center is larger for tap water images.

For the global images of tap water considering all measured parameters the mean CV is 1% and for Gelsemium 4%.

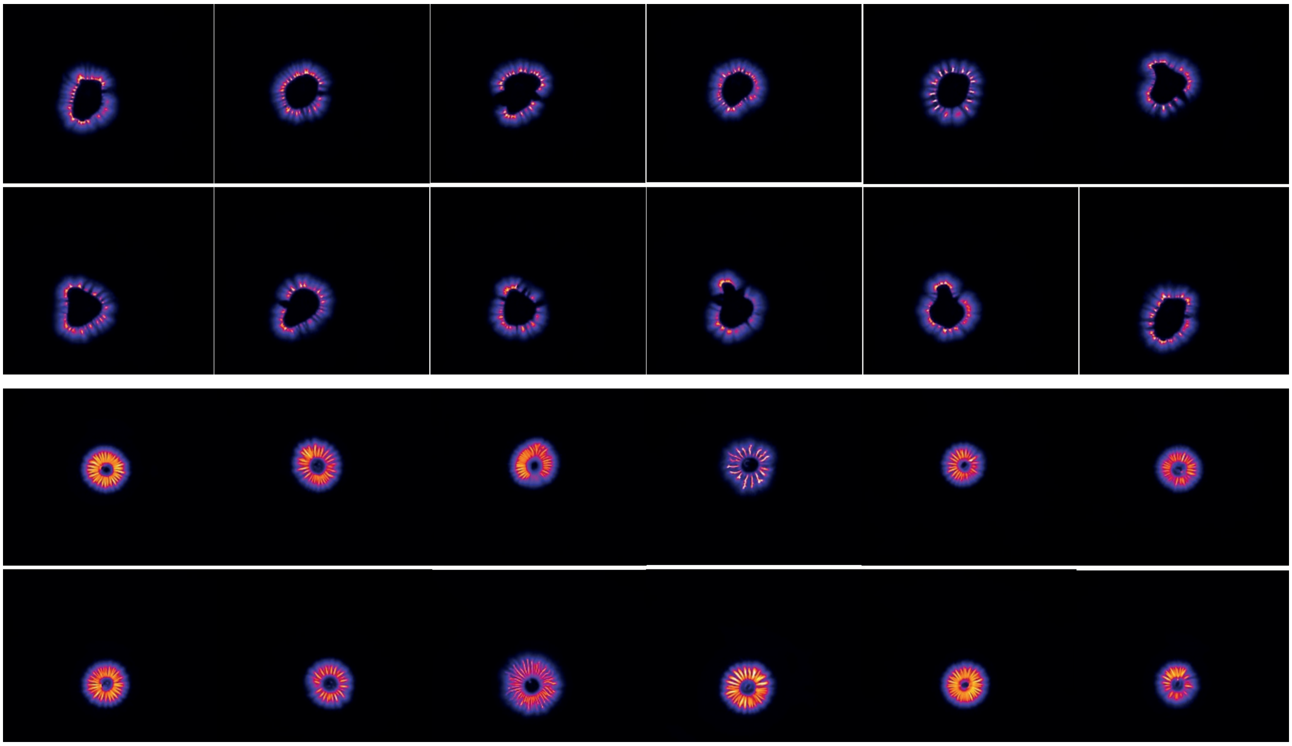


Figure 7: *12 images of drops of tap water above and below 12 images of high diluted Gelsemium.*

As the images are circular in shape, the angle values (or related parameters) are irrelevant when it comes to the selected external or internal area of Gelsemium, just like they are for tap water.

Considering the other parameters, during the area selection process, the variability of measurements is greater for Gelsemium than for tap water. The other parameters will also be affected by the instability of the size of Gelsemium images. The coefficient of variation for all parameters in the two selected zones (external and internal) is around 38%. Therefore, the size of the internal area needs to be normalized before the other parameters can be analyzed (Table 6).

Using a 2-way ANOVA (product/samples) for the external area, the normality and variance tests were passed for almost all parameters. Discrimination between products is statistically significant. For 26 parameters even at p<0.001. Among the 12 samples of each product, no significant difference can be observed.

For the internal area, results are the same, discrimination between products is statistically significant everywhere, for 27 parameters even at p<0,001.

D/ FFT images are focused on light wavelength of emitted light and do not need to go through a normalization process (Figure 8). The center corresponds to a large spatial wavelength. Wavelengths become shorter and shorter towards the periphery.

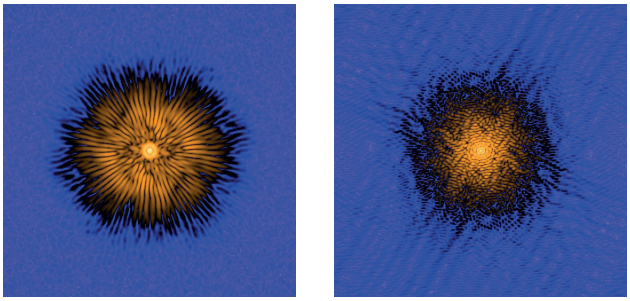


Figure 8: *On the left is an FFT image of a highly diluted Gelsemium drop. On the right is an FFT image of a drop of tap water, for example.*

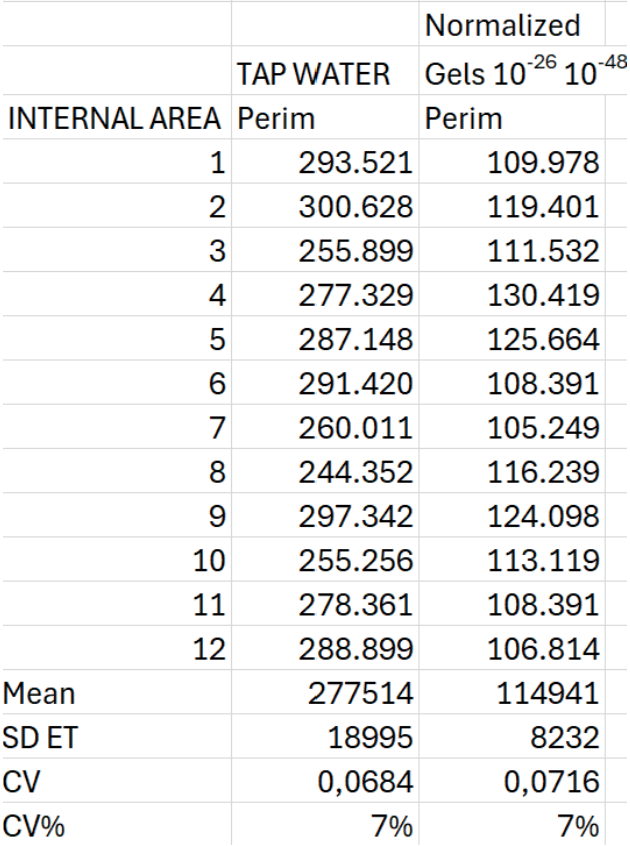
The first observed result is that all the FFT images of Gelsemium dilutions have only 2 central concentric zones (Fig 8) before streamers are expanding outside, just like pure ethanol (Fig 6). On the contrary, the FFT images of the tap water are more complex in the center; the streamers have a different structure.

The differences in the wavelengths of the emitted light are obvious even without statistical analysis. Using 3-way ANOVA, the parameters related to the selection of the area are specific and the difference is highly statistically significant (p<0,001) for product and zone, but there is no statistically significant difference between the different samples of the same product (Perim; BX; BY;

Width; Hight; Major; Minor; Feret; MinFeret). The same result is obtained for the intensity of the emitted light expressed in pixels (StdDev; Min). Kurtosis is also discriminant.

Detailed ANOVA spreadsheets in **supplementary material**.

Table 6: *The coefficient of variation for tap water is spontaneously acceptable. To obtain comparable values for Gelsemium images, the perimeter of the selected internal area, corresponding to the perimeter of the observed drop, must be normalized before analyzing all other parameters.*



		Normalized
	TAP WATER	Gels 10^{-26} 10^{-48}
INTERNAL AREA	Perim	Perim
1	293.521	109.978
2	300.628	119.401
3	255.899	111.532
4	277.329	130.419
5	287.148	125.664
6	291.420	108.391
7	260.011	105.249
8	244.352	116.239
9	297.342	124.098
10	255.256	113.119
11	278.361	108.391
12	288.899	106.814
Mean	277514	114941
SD ET	18995	8232
CV	0,0684	0,0716
CV%	7%	7%

5. CONCLUSION

The electro-photonic analytical approach is a valuable tool for gaining theoretical insights into chemistry. There are several reasons why these insights can be validated in practice. This validation needs to be confirmed using more data.

- The photographs of different samples of the same composition show reproducible results with a reliable coefficient of variation, which is a significant advantage of the method.
- The approach can detect measurable differences in the concentration of two comparable high-ethanolic solutions (with or without added material), which is important for achieving experimental accuracy.
- Even when the internal area, corresponding to a different volume of the drop has to be normalized, the method can distinguish between common tap water and highly diluted plant extract (Gelsemium).

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7. CONFLICT OF INTEREST

No conflict of interest.

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Ethical Issues in Communication of Chemistry

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Abstract. The present manuscript aims to present several ideas and reflections about ethical issues in chemistry communication, which represent a deepening and updating of an oral presentation at the Symposium of EUCHEMS working party "*Ethics in Chemistry*", held in Rome the 6th-7th July 2017. These concepts could be useful for the community of chemists to face future challenges concerning the relationship between Chemistry and Society. Some basic features of modern science, communication and communication of science are presented, since they represent an important framework to build a discourse about ethics in chemistry communication. The specificity of chemistry, such as its features as inductive, creative, flexible, transversal and central science, need to be considered by chemists to be aware of ethical issues specific of chemistry. In the present paper I discuss some ethical issues related to the communication of chemists within the scientific community, such as scientific publishing and artificial intelligence uses, and some ethical concerns related to the communication to the general public and the effect on the society of unethical communication related to topics such as sustainability, food, health and environmental impact of chemical research. The manuscript end with some reflections about the need of ethics of chemistry in chemists' training.

Keywords: Education, Chemistry, Ethics, Chemistry Communication, Ethics of Research; Ethics of Science, Science Communication.

1. INTRODUCTION

The present contribution aims to present several concepts and ideas about the communication of chemistry and related ethical issues, that could be useful for the community of chemists. This topic has been object of an oral presentation at the Symposium of EUCHEMS working party "*Ethics in Chemistry*", held in Rome the 6th-7th July 2017.[1] Before presenting and discussing the ethical issues related to the communication of chemistry, a brief introduction concerning science, communication and ethical aspects related to the communication of science will serve as a framework of the discussion.

1.1 What is science?

The starting point of the discussion about ethics in communication of science implies sharing some key features about what science is. Despite several definitions of science exists, and different sociological and philosophical theories still debate about the definition of science, there are several features that characterize science, in particular, modern science:[2-4]

1. Science is a systematic knowledge and a process for producing knowledge, that is characterized by several shared procedures (i.e. ask a question, make an experiment and collect data, interpret data, formulate hypothesis to be validated – or falsified, develop models, theories, and so on…), usually referred to as 'scientific method';[5]
2. Science is a collective human enterprise, since scientific knowledge is built up through the collaboration of scientists from many countries, working in an interconnected way;[6]
3. Science is social, in several senses, either because it is based on social relations among scientists or because of the social values of the research results;[7]
4. Science aims to share knowledge to everybody, without preserving secrets inside the scientific community, but, on the contrary, trying to build the larger consensus in the public and in the society. This is also at the basis of the idea of '*open science*'.[8]

If we accept these basic features, it is not surprizing that scientists need to communicate to the general public, without delegating it to others.

There are also other aspects of the actual status of modern science that support and justify the idea that scientists should take care about communication of science to the general public:[2]

a. Large amount of money is devoted to science and technology (within the national budgets, which varies sensibly from one country to another), so scientists need to justify their work, disseminate their results, and so on.

b. The number of scientists and researchers is increasing rapidly (for instance, with respect to the previous century), so the impact of the scientific community in the society is increasing.

c. The number of publications is increasing exponentially in the recent decades, and this opens several problems in the transfer of new knowledge to the public, who can be disoriented by this large amount of data, results, and information.

d. The presence of private companies and investors in science and technology is a reality, and this implies a major need and care in the communication of scientific results.

e. The scientific community expanded in all competing continents and the scientific knowledge has a global and international dimension.

1.2 Communication as an essential human activity

A second aspect to consider in our discussion is the definition of communication. The origin of the term 'communication' is the Greek '*koinon*' which means 'in common', 'shared with others' and the Latin '*actio communicandi*' which can be translated as 'to give something to others, sharing a gift with the community'.[9] The modern theories of communication[10] are in agreement with these ancient terms, since the communication is seen not as a simple transfer of messages from A to B: the nowadays accepted definition of communication implies feedback from B to A. According to this point of view, to communicate means to establish a common space with an exchange of information between individuals through a common system of signs, codes and languages. Communication has the aim to establish a relationship among individuals with shared objectives. The bidirectionality of the communication is indeed related to the social value of the communication. Among the theories of communication,[9] the ideas developed by G. Bateson[11] and later formulated by P. Watzlawick[12] and the Palo Alto school can be considered an important starting point for the development of a discourse about ethics of communication. According to them, five axioms of communication can be defined:

1. It is not possible not to communicate. Communicating is indeed an essential human activity. Even when we are silent, we are communicating something.
2. Communication has always two levels: one is related to the content, and the other one is related to the relationship between the communicant and the others.
3. The nature of the relationship depends on the structure and the sequence of communication itself. This means that the meaning of communication can be influenced by the punctuation of the communication sequence.
4. Human communication involves both digital (verbal, symbolic, …) and analog (non-verbal, emotional, …) forms of communication.
5. All communications can be classified as symmetrical or complementary. The symmetry or asymmetry are referred to the communicant and others.

1.3 Scientists need to communicate

With these premises, it is rather obvious that scientists need to communicate their works, disseminate the scientific results, take care in establishing a good relationship with their publics. Moreover, in the nowadays world, scientists have to face an increased complexity of tools and possible ways of communication. The digital world offers new possibilities, but, at the same time, the variety of tools implies the need of specific expertise. This topic is currently object of several intense research.[13]

Scientists need to communicate in first person, and they cannot delegate to others. At least, they cannot neglect or lose interest about this important activity. This is what Tim Radford, a British journalist, wrote in Nature in 2011:[14] '*the case for scientists as inherently bad communicators is a canard*' or, in other words, there are no reasons to think that scientists are not good communicators and should not communicate. To support this idea,[14] Radford says that scientists have some 'natural gifts' such as enthusiasm, fundamental to engage the public, training in clarity and in observation, and, most important, they have the knowledge. All these aspects are necessary for a good communication of science. However, there are some problematic aspects, too, such as the academic publishing: the style, the formal language and the rules in publishing scientific papers move away scientists from an effective communication to the public. This last point is at the basis of the contribution by Garrett and Bird,[15] dealing with the main challenges of science communication. Scientists need to tackle a complex issue: they need to communicate to many different groups and individuals; not only they are usually concerned with the internal communication, which is characterized by very specialized languages and modalities, either informal (over lunch or in the corridor) or formal (talking during a conference or writing a review paper), but they have to share their knowledge with policy makers, educators, journalists and the general public. According to these authors,[15] the communication of scientific information behind the scientific community is particularly problematic due to the lack of a specific training. Doctoral students and researchers are indeed trained to write papers and grant proposals, not to talk to schoolchildren or to write educational papers. Another limit in the formation of the new generation of scientists is the great specialization of young researchers into tiny sub-disciplines. Social impact of science, as well as epistemological and philosophical reflections on science, and in general multidisciplinary and interdisciplinary approaches are normally not included or even discouraged in scientists' training.

Despite these intrinsic limitations, scientists need to communicate their work and their research to the general public and in doing that they have to front several questions:[16]

- What is the best way to communicate?
- What are the purposes of communication?
- What does it mean a good communication and what are the ethical issues related to communication of science?

1.4 Basic principles of science communication and ethical issues

Several philosophers and experts in science communication tried to give some answers to the above questions, and their suggestions can be of help for scientists. In a seminal paper Pietro Greco,[2] a recognized writer and journalist who left important reflections about science communication, wrote that a science communicator should follow these basic principles: be closer to the truth, try to be impartial, not to be interested and be universal. These features are close to the ethical values of science, as first proposed by Robert K. Merton, with the known "*mertonian norms*", commonly referred under the acronym CUDOS: communalism, universalism, disinterestedness, and organized skepticism.[17] These ethical norms act as guides how science should be carried out and, in some ways, they can be transferred from science to science communication, as suggested by Greco.[2] However, as stated by Medvecky and Leach,[16] these ethical norms are far from being practical and they risk being only theoretical guidelines. As underlined by Burrell,[18] science communicators, either scientists or professional communicators, should consider the principles of honesty and accuracy, since '*effective science communication bridges the gap between the scientific community and the public, fostering understanding, trust, and informed decision-making*'.[18]

Other important considerations come from the founders of "*ethics of communication*", such as the German philosophers Karl Otto Apel[19] and Jurgen Habermas.[20] In an interview given to the Italian journalist, Enzo Moreno, Apel,[21] explains that a key point of ethics of the discourse and ethics of the communication is a set of basic norms which should guarantee the parity and co-responsibility of all members of a community. In the context of scientific and technological discoveries, Apel supports the idea that scientists should be ethical in communicating their works (i.e. by using a transparent communication, by explaining the consequences of the scientific results in the society, and so on…) to help all individuals recognizing their co-responsibility. The theme of responsibility of scientists has been object of several reflections by many philosophers and sociologists. A significant contribution comes from the philosopher Hans Jonas, who defined several principles of responsibility that can be applied to scientists too.[22] One of his statements is: '*Act so that the effects of your action are compatible with the permanence of genuine human life*', which underlines the concept of '*responsibility for the future generations*'. This idea recalls other important concepts relevant in the present discourse about ethics of communication, such as the evaluation of risks connected with a research result, and the precaution principle, to make few examples. The scientists need to consider the relationship between "*what they say*" and "*what they really do*" (for instance, in describing scientific results, in showing the potentialities of research, the utility of a scientific result for humans, and so on).

Communication of science is dialogic and social, and these features are related to the definition of communication itself, as seen in the previous section. According to Bucchi and Trench,[23] in the recent two decades, science communication has been deeply influenced by social media and digital technology, so that different communication strategies have been developed. Interactive and dialogic approaches such as talking about science in science caffè, theatral pieces, TED talks, scientific blogs, open discussion about science and society in informal contests and citizen science projects put in evidence how new trends in science communication are growing, which well fit in the category of 'social conversations'.[23] The dialogic aspect of science communication has several potentialities, as underlined by Lerma-Mayer,[24] in overcoming problems related to the digital communication, such as the pervasive misinformation and the spread of unverified information. To successfully do that, it is necessary to recognise and face cognitive, sociocultural, and technological biases which influence how information is presented and consumed. '*The dialogue*, write Lerma-Mayer,[24] *emphasises the active engagement of the public in scientific discourse, acknowledging the role of the public in knowledge creation, from receiving information to actively participating and co-creating knowledge*'.

Another aspect of scientists' communication is indeed related to the purpose of communication. Most scientists disseminate their research results following the so called '*deficit model*',[2] which implies the idea that scientific information and knowledge should be transferred to the public, thus avoiding a dialogic communication. According to König *et al.*,[25] communicating scientific findings can have several purposes: foster trust, assist public opinion formation, support evidence-based decision-making, promote science understanding, elicit engagement and positive attitudes toward science. For instance, if the purpose of communication is to increase science understanding, a scientist should be more focus in educating the public developing a critical thinking rather than transferring dogmatic scientific contents. On the other hand, if the main purpose is to contribute to the formation of a public opinion concerning a scientific problem, such as the need of a medical protocol or a choice related to an environmental issue, social and cultural background of the audience has to be considered carefully. The difficulties in pursuing these goals are evident in some recent issues related to vaccines, stem cells, pesticides, chemical additives in foods, and so on. For instance, the lay public struggle to understand why scientists have different positions on a topic and has difficulties in accepting the complexity and the uncertainty which is inherent of on-going research. Sometimes, there is a big mismatch between "*what scientists think is important to communicate*" and "*what the public is willing to know*" and this aspect has to be taken in mind when analysing the reasons of unsuccessful communication.[25] In addition to different aims and contents, scientists need to consider their audience, choose carefully the communication format and adapt their language accordingly.[26] As underlined in the previous section, one of the axioms of communication is related to the symmetry, or complementary, of the relationship between the communicant and the public. In the case of science communication, a structural asymmetry between the amount of knowledge of a scientist about a specific topic he/she wants to communicate and the lack of knowledge of the lay public is inherently present. This aspect represents a limitation which should be overcame to move towards a more symmetric relationship which is a fundamental aspect of ethical communication.[9]

2. ETHICAL ISSUES IN CHEMISTRY AND CHEMISTRY COMMUNICATION

In the previous section, some basic features of science, science communication and ethics of science communication according to the literature on these topics have been briefly reported to build a framework for the discussion about the specificity of chemistry. As it will be shown in the next pages, some aspects of ethics of communication of chemistry are common with other scientific disciplines. However, chemistry presents several distinctive features which merit to be discussed to understand ethical implications of chemistry communication.

2.1 The nature of chemistry and ethical implications

The first reflection concerns the nature of chemistry and the features that characterize chemistry with respect to the other scientific disciplines. As Jeffrey Kovac asks rhetorically in his work,[27] '*What makes chemistry unique? And how does this uniqueness reflect on chemistry's unique concerns with ethics?*' His answer includes a simple consideration: chemical systems are at the right size to affect humans directly, since the object of chemistry are substances, at the macroscopic level, and molecules, at the sub-microscopic level. In this sense, chemical objects are intermediate between the very small and the vary big, and they interact directly with our perceived world.[27]

Frank *et al.*[28] described the three principal characteristics of chemistry that distinguish this science from other disciplines: the inductive character of chemical knowledge, its creativity and flexibility.

2.1.1 Chemistry as inductive science

The first feature is related to the inherent experimental nature of chemistry: observations and experimentations following the scientific method were at the basis of the understanding of many chemical phenomena, either natural or artificial ones. In particular, some branches of chemistry, such as inorganic, organic and pharmaceutic chemistry, have developed through the history thanks to the inductive approach. The experimentations are related to some important ethical issues, such as the need (or not) of animal experiments to develop new drugs.

2.1.2 Chemistry as creative science

Creativity is probably the most crucial aspect in terms of ethics. It attains to the ability of chemists to design and produce new chemical substances, not existing in nature, with potential negative effects on humans and on the environments. This can be a real big problem, since chemists synthetise thousands of new compounds every year. Even though they are produced to benefit the humankind, to solve problems related to the environment or to the health, nobody can exclude their eventual negative impact after many decades or their use for different, even dangerous, applications with respect to the initial aim. Several interesting cases are reported in the special issue of Hyle published in 2016.[29] Ruthenberg discussed the ontological underdetermination of chemicals, in particular of bioactive compounds, starting from the historical and famous case of the thalidomide.[30] In this story, a role was also played by the way thalidomide healthy effects were communicated. As Ruthenberg[30] reports this drug was advertised excessively, and, in particular, two aspects were emphasized in the marketing campaign: the lack of toxicity and the natural ness of the support of a 'good sleep'. In this case, as Ruthenberg[30] states, chemists had several responsibilities, in fact '*neglecting the underdetermined chemical character of their product, they decided to follow or tolerate an aggressive marketing campaign based on at least incomplete and distorted results and trivialized or neglected all the anxious reports about side effects*'. Another interesting case is the one reported by Martin *et al.*[31] concerning the bisphenol-A risks. This case exemplifies the societal debate over the impact of industrial chemicals, since bisphenol-A (BPA), which was introduced in the market with the production of epoxy resins, is present in many consumer products such as baby bottles, reusable water bottles and food packaging, and it dissipates during multiple consume, thus potentially affecting a great number of humans. The estrogenic properties of BPA have been known since the early 1900s, however there were scientific controversies about their risks for health. This case is indeed an example of the difficulties in defining chemicals toxicity and of the roles of regulatory agencies and governments in the decision about chemicals' regulations.[31]

2.1.3 Chemistry as flexible science

The third feature of chemistry according to Frank *et al.*[28] is its flexibility, which refers to the fact that any new chemical substance or in general any new chemical knowledge open to many possible applications and unpredictable uses in many different areas, such as medicine, electronics, material science and technology, and so on. This concept is also related to the so called 'dual use', which means that a chemical substance synthesized for a particular purpose (to benefit humanity, such as a new drug for a specific disease) can be used for a negative purpose, criminal or military objectives, and vice versa. The duality of the use of chemicals is mostly related to applications, but it concerns either pure or applied chemistry.[28]

2.1.4 Technochemistry

The link between chemical knowledge and technology is nowadays so evident that the new term 'technochemistry' has been coined by Chamizo to describe this way of generating knowledge:[32] *'technochemistry then, refers to the activities derived from the chemical experiment, which in a fundamental way and based on a specific set of values, transform the reality in which we live'.* According to Chamizo, the concept of technochemistry opens to new questions which span from education to public understanding and finally to ethics.[32] The intimate relationship between chemical knowledge and real products as well as technology implies a high level of interdisciplinarity, and it supports the idea of chemistry as a transversal and central science.[33]

2.1.5 Chemistry as transversal and central science

The Nobel Prize in Chemistry Carolyn Bertozzi[34] wrote that the term "*central science is now widely used to describe chemistry's focal role in bridging the physical and life sciences, and the basic sciences with applied disciplines like medicine and engineering*". As argued by Chamizo and Ortiz-Millán,[35] since chemistry and its sub-disciplines '*are to fulfil their goal of generating knowledge and helping us solve the great challenges of the contemporary world, then it is morally imperative that scientists from different disciplines be more open to interdisciplinary work.'* Interdisciplinarity of the research, which implies a collaborative work among different disciplines is intimately related to the concept of transversality and centrality of chemistry, since '*chemistry plays a vital role in the materials, biomedical, environmental and energy sciences*'.[34] A consequence of these specific features of chemistry, according to Chamizo and Ortiz-Millán,[35] is that since an interdisciplinary approach is necessary to solve complex problems or to understand certain phenomena in reality, chemists have the obligation to pursue it.[35]

2.2 Domains of ethics in chemistry communication

As reported in the paper by Mehlich *et al.*[36] there are several ways of categorizing ethical aspects of chemistry: good or bad, right or wrong, clear cases or unclear ones. Another way is to distinguish ethical issues in chemistry in two domains: internal domain (concerning the individual chemists or the chemical community) and external domain (dealing with the impact of chemistry in the societal, environmental and economical levels).[36] In the following paragraphs I have used these two domains to describe the ethical issues related to chemistry communication. In particular, with the internal domain I intend the actions of both individuals and chemistry community having an impact mostly within the chemistry community (such as the misconducts in publishing or in mentoring), while with external domain I refer to those activities that have a direct impact on society (such as the exaltation of a scientific finding in a public arena or through the digital media). As it will be noted by the readers, this distinction is not always so net, and this will be commented case by case.

2.3 Ethical issues in communication of chemistry: internal domain

2.3.1 Scientific publishing

Examples of ethical issues of communication of the scientific results within the scientific community, pertaining to the internal domain, are related to the phenomenon of '*temptation to plagiarise, not acknowledging prior work to make own research appear more novel, falsifying data, publishing before ensuring reproducibility*' as reported by Nina Notman within her commentary.[37] These are ethical concerns linked to scientific publishing, and as a consequence to communication of science within the scientific community. It is known that this is one of the collateral effects of the so-called '*publish or perish*' system, which has determined the exponential growth of published scientific papers in the recent years as well as the emergence of new scientific journals by publishing houses: the so-called predatory journals. This publishing system is threatening the science credibility, and the fact that government institutions has introduced several indexes based on papers citations in the evaluation of scientists for their academic career, has determined some distortions, as reported in a recent paper by Baccini *et al.*[38] These phenomena concern chemists and chemistry, too. The retraction of scientific papers is related to these kinds of ethical concerns. An interesting paper dealing with the retraction of papers in chemistry was recently published by Sevryugina and Jimenez.[39] As shown in this work, the main reason for retraction of manuscripts published in the field of Chemistry is misconduct (58.5%), which includes several behaviours (frauds, plagiarism, self-plagiarism, and so on). In particular, self-plagiarism, such as the publication of part of already published works, or data, or the reuse of some figures or data without citing previous works, represents a relatively high percentage of misconducts (32.3%). However, as the authors underlined, we should consider that not all retractions are related to unethical attitudes by the authors, and that the retraction its-self should not be stigmatized, since it is *'an act of repair, an intrinsic part of the research lifecycle'*.[39] According to Koo and Lin, who performed a bibliometric analysis from 2003 to

2022 using Web of Science, '*retractions play a vital role in maintaining research integrity by ensuring the accuracy of the scientific record, promoting transparency and accountability, deterring misconduct, and fostering a culture of continuous improvement within the scientific community*'.[40] Retraction of published papers is a relatively recent phenomenon, which increased in the last 40 years of about 20%, probably due to an increased awareness to scientific misconduct and errors in the research community. Other important aspects in scientific publishing are reproducibility and data transparency.[41] The first feature is a fundamental element of science, since the process of validating and confirming scientific theories, which is a step of the scientific method, is based on the possibility to replicate published results. Transparency is another important aspect of scientific publishing, since, for instance, the description of synthetic procedures and the raw data used to elaborate or validate a structural molecular model needs to be accessible to other scientists. '*Confidence in scientific claims* – says Brian Rosek in ref. 41 - *is rooted in being able to interrogate the evidence for the claims and how that evidence was generated. Without transparency, the self-corrective processes of science are hampered*'. A recent paper by Ciriminna *et al.*[42] reports a study on reproducibility of chemistry research by analyzing papers and reviews in the fields of materials, supramolecular chemistry, electro-organic synthesis, and catalysis. Among the main findings reported in this paper,[42] the awareness of chemists and chemical journals of the need to improve reproducibility emerges. Even in chemistry-related topics - the authors write – '*the "publish or perish" principle contributes to the publication of non-reproducible results*'.[42] However, good practices introduced by several journals, such as the publication of supporting materials, the embedding of videos and photographs of experimental works, and the publication of online pre-print versions, could help in contrasting this problem. Improving scientific publishing in the open science and digital era is indeed mandatory for ethical communication of scientific results.

2.3.2 Artificial intelligence

Among the emergent ethical problems related to scholarly communication of science is the use of artificial intelligence (AI), such as ChatGPT,[43] which is largely used for educational and professional writing. As underlined by Brian L. Frye, the use of ChatGPT or any other AI text generators to produce academic writing is subject to several problems, such as plagiarims, which is defined as *the act of copying or closely imitating the work of another person or source without proper attribution or permission.*[43] Ethical considerations regarding the use of AI in writing and communicating science concern copyright, dishonesty, security and privacy issues. The acritical use of AI could decrease human creativity and engagement, and it could also exacerbate the digital inequality, disadvantaging people with low access to high-quality technology. A recent paper concerning the use of AI tools in chemistry and physics education has been published[44] showing the high potentialities as tutee, to solve problems, give comprehensive descriptions, support teachers in the assessment of students' knowledge. However, these tools can originate misinformation or create misunderstanding among students.[44] This topic will be probably at the basis of deep investigations in the next future.

2.3.3 Mentorship

Another ethical aspect related to the communication within the internal community regards the relationships among professors, scholars, researchers and students, and it is intimately connected with the general hierarchic structure typical of the academy. These imbalanced relationships brought to unethical behaviours, such as the episodes of abuse, bullying and discriminations that represent a problem '*in almost every country and every cultural realm*'.[36] However, these issues seem to be common with all academic disciplines with no specificity of chemistry with respect to other sciences.

As a final comment, what is interesting is that these ethical concerns, which are mainly related to the internal domain of chemistry communication according to the initial definition, affect the public image of chemistry, too. In this sense, controverses, misconducts and unethical behaviours have severe implications in the external domain.

2.4 Ethical issues in communication of chemistry: external domain

2.4.1 Chemists and Society

The communication of chemistry to the general public and the perception of chemistry in the society are considered crucial by most of Chemistry Societies, from the national ones to the international IUPAC (International Union of Pure and Applied Chemistry).[45] The image of chemistry in the society changed during the history, in particular, in the last two centuries when this science has become central and strongly interconnected with technological developments.[32] The reasons at the basis of the perception of chemistry in the society nowadays are quite complex and they have been object of several investigations in the recent years.[46-48] Despite of this inherent complexity, several reasons have been identified,[49,50] such as the way chemistry and chemical concepts are taught at school levels, the history of chemistry as modern science and the intrinsic nature of chemical concepts, the intimate relationship between chemical research and the chemical industry as well as the way chemistry-related topics have been communicated in the past and in the present. As previously reported,[29-31] there are some significant historical cases, such as the thalidomide story, the Bhopal disaster[51] and the Seveso accident,[52] which strongly affected and modified the public opinion toward chemicals and chemical industry. These events had a great impact on the society and the way they were communicated to the public had consequences on the perception of risks associated to chemicals and chemical industry. Since the sixteenth, with the fundamental book titled '*Silent Spring*' by Rachel Carson, the sensitivity of the publics towards the environment and the effect of human activities on it, raised and this change in behaviour affected the perception of chemicals and their potential negative effects on the environment.[53,54] In this case, the role of communication is very exemplary, for the media resonance of Carson's study on one side, and for the silence or, even worse, for the incoherent reaction of the chemistry community on the other side. Based on these cases, chemists should reflect on the role of communication of chemistry-related topics having a strong impact on the health, environment and safety.

As underlined by Mehlich *et al.*[36] the role of chemistry on sustainable development should be communicated in a more responsible and accurate way. Moreover, when communicating their research results, chemists should be aware that the public image of chemists is different from their self-image, as pointed out by Laszlo.[55] In fact, the goodness of research aims, the honesty of chemists, their attention to the environment and to the safety and the utility of chemistry researches are far from being obvious to the general public, instead these aspects should be communicated. As pointed by Hartings and Fahy,[56] to improve the effectiveness of chemistry communication, chemists should build a positive and trusting relationship with the public. The diffuse lack of public engagement with chemistry is indeed a well-known problem, as it will be treated in the next paragraph.[57-59] A suggestion for chemists could be to adopt the '*mertonian norms*', not only when doing their research but also when communicating chemistry results. The choice of an adequate language, without oversimplification of the real problems, without hindering the risks and implications of new forefront research results are additional ethical implications.

2.4.2 Fake news, misinformation and conflict of interest

Fake news represents one of the biggest problems in science communication due to the exponential grow of information with internet and social networks.[58] The diffusion of misinformation and false news about science is not new: there are some famous historical cases, such as the publication of pseudoscientific information reporting positive and negative effects on health related to the new discovered X-ray.[60] However, the amplification of pseudoscience and misinformation through the web and with the social networks is certainly increasing the impact of fake news in the Society. Fake news affects chemistry too, and chemists are directly involved in the important work of reducing the spread of misinformation concerning chemicals and mitigating the discussion around the potential positive or negative effects of chemistry. A known problem which was reported by several authors[48,58,61] is related to food chemistry. Misinformation about healthy or unhealthy properties of food and agricultural products (see the case of pink salt) are often related to scientific publications which hinder unethical behaviours, such as conflicts of interest, in the case one or more authors received funding from private companies which profit based on those scientific results. The public perception of chemicals, such as food additives,[61] and of natural products, such as organic food, is highly influenced by marketing communication, which tends to introduce scientific terms to justify or make stronger a message, by using communication strategies, such as logic constructs and inferences, that have not a scientific basis. Chemists should be not complicit of this unethical way of communicating, especially when presenting their scientific results to the public, through interviews or institutional press releases. Moreover, as put in evidence by Shim *et al.*,[61] since safety perceptions of chemicals are affected by consumer awareness and knowledge, more efforts in chemistry communication and education are necessary.

At the end, some simple suggestions for chemists who wish to get a better and more ethical communication could be: 1. Before starting the communication: ask themselves some basic questions, such as: what is the aim of my communication? Who is my target? Why the public should be interested in my research? 2. Spend some efforts in building a critical approach in the public, thus avoiding dogmatic speeches and idealistic description of science, talking about the scientific methods, the complexity of a phenomenon, and the intellectual controversies around a scientific topic; 3. Communicate the research works and activities as a human activity, trying to establish an empathy with the public, preferring a dialogic and interactive approach; 4. Put more attention to the choice of language to communicate to the public (i.e. the use of less technical words instead of very specific ones); 5. Be honest.

2.5 Ethics of chemistry and chemistry communication in chemists' training

Before concluding this paper, it could be useful to reflect about the presence of these topics in chemists' training, since, as stated by several authors, chemists are expected be prepared to reflect on the social values related to chemistry results.[29] To this aim, ethics of chemistry should be included in the training of chemists as an obligatory undergraduate course in all Universities.[36,62,63] Few good examples of preparing ethical chemists through courses at university level have been reported,[64-66] however these are rather isolated cases. Several years ago, the *EuChemS* working party about *Ethics of Chemistry* developed a modular course entitled '*Good Chemistry: methodological, ethical and social dimensions*' and a very useful book containing theory and practical examples was published by Jan Mehlich.[67] Part of these materials was experimented at the Jagiellonian University in Krakow within a MOOC course.[64] Among the selected topics, scientific misconduct, responsibility, risk, uncertainty and precaution principles were declined to deal with ethical issues in chemistry. As stated by Maciejowska,[64] the module dedicated to science communication was particularly appreciated by students: '*Students comments on the forums of this MOOC showed that there is a continuous need to develop communication skills, including engaging in scientific discourse about responsible research and innovation, particularly within STEM programs*'. Communication skills was one of the topics addressed in the chemistry courses described by Singiser *et al.*[65] and by Baker Jones and Seybold:[66] the objective of the lessons and activities was to provide students adequate tools for communicating within the science community (internal communication). For instance, some sections were dedicated to the scientific presentations (oral, written or poster types) and the scientific discussions among peers.[65] More specific ethical reflections about the scientific research and its historical, political and social implications, are addressed in the course of '*History of Chemistry and Didactic aspects*'[68] which is hold at the University of Pisa since 2018. Within this course,[68] the history of the disputes around the discovery of several chemical elements is taken as representative of several critical aspects of ethics in chemistry, such as the gender discriminations and discriminations based on the nationality, the ethics of publishing and communicating the scientific results.

3. FINAL CONSIDERATIONS

In the present contribution, I have discussed some aspects about ethics of chemistry communication, starting from the analysis of specific features of chemistry and ethical implications. The discussion of ethical issues concerning communication of chemistry was divided between the communication of researchers within the scientific community, covering, in particular, the ethical aspects of scientific publishing, and the communication of chemists to the public, with a direct impact on the image of chemistry in the society. The role of misinformation, fake news, conflict of interest and dishonest communication on the perception of chemistry and chemists in the society has been discussed. In the recent years there have been several signs in the community of chemists of an increased attention on chemistry communication. The Royal Society of Chemistry[54] was pioneer in 2015 with a first systematic and detailed investigation on how chemistry is perceived in the general public, with the aim to produce a practical communication tool kit for chemists. More recently, the Italian Society of Chemistry[55] started a program of innovation in the communication of the role of chemistry in the society, trying to contrast to the diffusion of fake news and putting more attention to the education of young students to get them involved with chemistry. However, in the academy, these topics are still considered marginal with only few exceptions, revealing a substantial lack of a specific training of the academic staff in science communication and a relatively low sensitivity toward communication and education, probably because these topics are still not considered central and not adequately recognized.

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Research Article

Scientia and Transformation

Rethinking Medieval Science through Alchemy and Natural Philosophy

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Abstract. This study introduces a new framework for understanding medieval science by recognizing alchemy as a central mode of rational inquiry. Through the integration of theoretical reflection and material practice, alchemy shaped a vision of nature governed by intelligible processes and oriented toward perfection. The contribution of this work lies in its demonstration that medieval alchemical knowledge operated through experimental attention. Rather than isolating observation from metaphysical purpose, it forged a unified method where transformation became the pathway to understanding. By highlighting this coherence, the study redefines the historical foundations of chemistry and restores to alchemy its formative role in shaping scientific imagination.

Keywords: Alchemy, Medieval Science, Natural Philosophy, Epistemology, Transformation

INTRODUCTION

To approach the notion of science in the medieval period is to enter a terrain shaped as much by modern prejudice as by historical complexity. For centuries, the dominant narrative has cast the Middle Ages as an intellectual interregnum, wedged between the scientific clarity of antiquity and the rational awakening of the modern world. This view—fueled by Enlightenment rhetoric and the nineteenth-century cult of progress—has proved remarkably persistent, though recent scholarship has challenged it with increasing force. What emerges from a more nuanced reading of the sources is a landscape of scientific inquiry that was neither static nor wholly subordinate to theology. Rather, it was dynamic, internally diverse, and intellectually ambitious, even as it operated under metaphysical constraints unfamiliar to the modern scientific mind.

Yet medieval science was not "science" in the contemporary sense of the term. It lacked, for the most part, systematic experimentation and quantitative modeling. It did not seek falsifiability or empirical autonomy. What it did possess, however, was a coherent and often elaborate framework for understanding nature, rooted in classical philosophy, transmitted through Arabic and Latin traditions, and reshaped by Christian theological demands. Within this framework, disciplines that today would be considered separate—astronomy, medicine, natural philosophy, even what we now call chemistry—were united by the ambition to uncover the causes and principles governing both the heavens and the earth.

Alchemy deserves special attention here—not as a marginal or deluded cousin of chemistry, but as a legitimate mode of investigation situated at the intersection of matter, spirit, and transformation. Far from being a dark corner of medieval thought, alchemy represented a serious intellectual project. It operated with its own theoretical vocabulary, drew from Aristotelian and Neoplatonic ontologies, and relied on laboratory practices that, while symbolically encoded, were grounded in observation, manipulation, and change. The work of transmutation—of transforming base substances into noble ones—was not merely a quest for gold but a philosophical and often spiritual undertaking, in which the purification of matter mirrored the refinement of the self. That the history of chemistry is inseparable from this tradition is not a matter of accident but of genealogy.

To address these issues, it is essential to draw on studies that provide a scientific framework for understanding the premodern period. Two scholars in particular have developed a general framework for reflecting on the subjects under investigation: Pamela H. Smith and Pamela O. Long.

Pamela H. Smith has made significant contributions to the understanding of premodern science by emphasizing the central role of material experience and artisanal practice in the production of knowledge. Her work highlights how technical expertise was not peripheral to natural philosophy but often served as its empirical foundation, mediated through complex cultural and textual processes. At the core of her approach is the figure of the artisan as an epistemic agent, capable of translating lived experience into conceptual frameworks, methods, and scientific representations[1].

Pamela O. Long, on the other hand, has focused on the intersections between mechanical arts, technologies, and theoretical knowledge in premodern Europe. She has shown how the boundaries between these domains were fluid and mutually influential. Her scholarship underscores the intellectual value of so-called "lower" or practical arts, arguing that they played a crucial role in shaping early scientific thought. Through a historical-epistemological lens, Long challenges traditional hierarchies of knowledge and repositions technical practices as fundamental to the development of scientific culture[2].

A special mention should be made of Sébastien Moureau, regarded as one of the leading experts on Arabo-Latin alchemy. His research has focused on the transmission of Arabic alchemical texts into medieval Latin culture, highlighting the role of translators and the circulation of manuscripts. Moureau's work is particularly valuable for its philological precision, which allows a clearer understanding of how technical terminology and symbolic language were adapted across linguistic and cultural boundaries[3].

This essay does not aim to redeem medieval science in a triumphalist way, nor to romanticize its limitations. Rather, it seeks to examine its epistemic foundations, institutional settings, and material practices, while drawing particular attention to the often-overlooked role of alchemy and proto-chemical experimentation. By comparing the medieval conception of knowledge with that of modern science, we may not only gain a more accurate historical picture but also challenge the assumptions that govern how we define science today. Each chapter will examine a different dimension of the medieval scientific worldview: its epistemological premises, the institutions and figures that shaped it, the domains of inquiry through which it operated, and finally, its most speculative and transformative practices—especially those tied to alchemy and the manipulation of matter.

CHAPTER 1: KNOWLEDGE AND METHOD IN THE MEDIEVAL SCIENTIFIC IMAGINATION

To speak of "science" in the Middle Ages is already to risk anachronism. The Latin *scientia* denoted not a discrete field of empirical inquiry, but rather a form of systematic knowledge: demonstrable, coherent, and ordered according to rational principles. This knowledge was understood primarily in Aristotelian terms—as a syllogistic structure, deduced from first principles and oriented toward certainty. It was not about discovering the unknown through experimentation, but about

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[1] Pamela H. Smith, *From Lived Experience to the Written Word: Reconstructing Practical Knowledge in the Early Modern World*, The University of Chicago Press, 2022.

[2] Pamela O. Long, *Artisan/Practitioners and the Rise of the New Sciences, 1400-1600*, Oregon State University Press, 2011.

[3] Moureau Sébastien, *Min al-Kīmiyā' ad Alchimiam. The Transmission of Alchemy from the Arab-Muslim world to the Latin West in the Middle Ages* in *Micrologus 28. The Arabic Sciences in the Western World*, edited by Charles Burnett, Danielle Jacquart, and Agostino Paravicini Bagliani, pp. 87–141; Moureau Sébastien, *Laboratories and Technology: Alchemical Equipment in the Middle Ages* in a *Cultural History of Chemistry*. Vol. 2. Middle Ages, edited by Charles Burnett and Sébastien Moureau, 49–70, London: Bloomsbury, 2021.

articulating what could be known by necessity. In this sense, *scientia* was closer to geometry than to modern chemistry, though it applied itself to questions ranging from the movement of the stars to the functioning of the human body. And yet, despite this deductive orientation, medieval thinkers did not dismiss observation; they simply subordinated it to theoretical clarity.

Thomas Aquinas's engagement with Aristotle offers a paradigmatic case. In his *Commentary on the Posterior Analytics*, he interprets demonstrative knowledge as that which begins from causes "better known in themselves," moving logically toward conclusions "better known to us".[4] This reversal—starting from ontological priority rather than empirical data—encapsulates the medieval commitment to metaphysical realism. Knowledge was not constructed from observation upward, but derived from universal truths downward. Scientific thinking, in this light, was deeply theological, because it presupposed a rational cosmos whose structure could be deciphered precisely because it was created by a rational God[5].

This orientation had real implications for how natural phenomena were investigated. In natural philosophy, the question was not merely *what* happened, but *why*—in the strongest, causal sense of the term. Explanations sought formal and final causes, not just efficient ones. Fire rose not only because of its lightness (in Aristotelian physics), but because its nature was oriented toward the heavens. The alchemist, too, operated within this metaphysical framework. When he heated a substance or dissolved it in acid, he was not simply producing reactions: he was, ideally, unveiling its hidden nature, moving it toward its perfected state. Matter was never inert. It had tendencies, orientations, even a kind of metaphysical yearning. The furnace, in this context, became a site not only of transformation, but of revelation[6].

In contrast to modern scientific methods, the medieval world lacked standardized experimentation or statistical verification. Yet there were forms of repeated practice, especially in disciplines like alchemy and medicine, that produced cumulative bodies of empirical knowledge. The alchemist's operations—*calcination*, *coagulation*, *distillation*—were codified through experience, even if framed in symbolic or cosmological terms. What we might recognize today as chemical insight was mediated through a language of correspondences, analogies, and hidden signatures. To modern ears, the language of *sulphur* and *mercury* as elemental principles may sound opaque or even fantastic. But these were attempts to theorize material properties in dynamic terms: activity, volatility, fixity[7]. If modern chemistry emerged from this tradition, it did so by slowly stripping away its metaphysical scaffolding, not by rejecting its empirical core.

It is also worth noting that medieval thinkers were aware of the epistemological limits of their system. Robert Grosseteste, in the 13th century, argued for a form of experimental testing—not as a challenge to authority, but as a means to clarify the principles laid down by reason and tradition[8]. His treatise *De luce* attempted to reconcile metaphysical principles with geometric optics, suggesting that light was the fundamental agent of natural causation. Though this did not result in a full experimental program, it reveals a restlessness within the system—a sense that reason alone might not suffice.

Still, the boundary between speculative and empirical remained porous. In the alchemical texts attributed to pseudo-Geber, one finds a mixture of precise laboratory procedures and allegorical language. Recipes for the preparation of aqua regia or for the sublimation of mercury sit alongside claims about the spiritual purification of the operator. These texts were not irrational; they operated according to a different rationality—one that treated nature as intelligible not only through mathematics and logic, but through analogy, moral order, and even sacrament[9].

In sum, the medieval conception of scientific knowledge was not anti-empirical, but embedded within a metaphysical worldview that shaped how knowledge was defined, pursued, and justified. It did not aim to separate the knower from the known, but to harmonize the two within a cosmos charged with purpose and hierarchy. While this approach differs radically from the procedural skepticism (scepticism?) of modern science, it was neither static nor simplistic. It generated systems of thought—particularly in alchemy and early chemistry—that, for all their symbolic opacity, rested on genuine engagement with the material world.

CHAPTER 2: INSTITUTIONS, TRANSMISSION, AND THE MATERIAL INFRASTRUCTURE OF SCIENCE

Scientific knowledge in the medieval world did not circulate freely or chaotically. It required structures—

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[4] Thomas Aquinas, *Commentary on the Posterior Analytics*, trans. Larkin, Dumb Ox Books, Notre Dame, 2009, I.2 (72a1–5).

[5] Edward Grant, *God and Reason in the Middle Ages*, Cambridge University Press, 2001.

[6] Lawrence M. Principe, *The Secrets of Alchemy*, University of Chicago Press, 2013.

[7] William R. Newman, *Atoms and Alchemy*, University of Chicago Press, 2006.

[8] David C. Lindberg, *The Beginnings of Western Science*, University of Chicago Press, 2007.

[9] William R. Newman, *The Summa Perfectionis of Pseudo-Geber*, Brill, Leiden, 1991.

material, intellectual, and institutional—capable of preserving, transmitting, and sometimes transforming complex bodies of thought. From the scriptorium to the university, from the apothecary's workshop to the private study of the alchemist, medieval science took shape within defined spaces and under particular conditions. To reduce these institutions to mere containers of ancient knowledge, as earlier historiography sometimes did, is to miss their function as active agents in the development of intellectual life.

Alchemy, in particular, moved in and out of academic respectability. While formal chairs in alchemy did not exist, alchemical texts were studied by university-trained thinkers, including Albertus Magnus, who treated them as part of natural philosophy. His *De mineralibus* includes passages clearly indebted to the Arabic alchemical tradition, and while Albertus remained cautious, his engagement was systematic. He even attempted to classify various chemical operations, noting the role of heat, dissolution, sublimation, and fixation—not as mystical gestures, but as methods of altering substance[10]. What is more, university libraries began to collect alchemical manuscripts, including Latin translations of works attributed to Jābir ibn Ḥayyān, pseudo-Aristotle, and Hermes Trismegistus. These were read not as occult curiosities, but as serious—if symbolically rich—attempts to understand material change.

It would be misleading, however, to limit the history of medieval science to universities alone. Much of the hands-on work of observation, especially in the domains of medicine and chemistry, took place elsewhere: in apothecaries' shops, in the studios of glassmakers, in metallurgical sites, and, crucially, in private laboratories. The boundary between scholars and craftsmen was permeable. In some cases, they were one and the same. The alchemist had to know not only Latin and Aristotelian theory, but also how to manage heat, measure timing, handle corrosive substances, and work with rudimentary distillation apparatuses. The so-called *aludel*, the *athanor* furnace, and the *pelican* still were not philosophical metaphors—they were physical tools requiring skill and familiarity[11]. These techniques prefigure what would become laboratory science. And yet, because they were often embedded in a symbolic language of transmutation and spiritual purification, their status remained ambiguous within academic circles.

Transmission also mattered. The so-called "Toledo Translation Movement" of the 12th century brought a flood of Arabic texts into Latin Europe—not only philosophical works but also medical, astronomical, and chemical treatises. The translation of alchemical texts was particularly delicate, given the symbolic density and terminological instability of the originals. Translators had to make decisions: how to render *elixir*, or *iksir*? These choices affected how generations of Latin readers interpreted the operations of (the) matter. In some cases, translation was also interpretation—an act of synthesis or even revision[12].

This infrastructure—of texts, tools, institutions, and translation networks—enabled a form of scientific life that was less experimental than modern science, but no less methodical. It is not that medieval scholars did not observe; they are observed within frames shaped by inherited metaphysics, institutional hierarchies, and textual authority. The alchemist, manipulating substances by fire, was not violating the norms of knowledge; he was expanding them from within. That later generations would draw a line between chemistry and alchemy does not mean the line existed in the 13th century. In that world, to understand the world was also to transform it—and possibly, in doing so, to redeem it.

CHAPTER 3: TRANSFORMING NATURE — ALCHEMY, EARLY CHEMISTRY, AND THE PRACTICAL PURSUIT OF KNOWLEDGE

If the medieval world imagined knowledge as the discovery of order, it imagined nature as something that could be perfected. Alchemy, far from occupying the fringes of medieval thought, offered one of the most sustained and technically sophisticated explorations of that possibility. It was not, as modern caricatures would have it, a naïve hunt for gold by charlatans in smoky chambers, nor was it merely a metaphorical language for spiritual ascent. It was a hybrid practice, combining close material observation with speculative reasoning, a practice that blurred the boundaries between what we now separate as chemistry, medicine, metaphysics, and even theology. To follow the alchemist in his laboratory—not merely through symbolic diagrams but through crucibles, furnaces, and volatile materials—is to enter a world in which matter and meaning were in constant negotiation.

By the thirteenth century, Latin Europe had access to an increasingly rich corpus of alchemical texts. Some came from the Arabic tradition, others were pseudoepigraphic, attributed to Hermes Trismegistus, Aristotle,

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[10] Albertus Magnus, *De mineralibus*, in Borgnet, ed., *Opera Omnia*, Vivès, Paris, 1890.

[11] William R. Newman, *Promethean Ambitions*, University of Chicago Press, 2004.

[12] Charles Burnett, *Alchemy and Arabic Science*, Variorum, Aldershot, 2001.

or even Moses. What they shared was a conviction that all matters were in motion, not chaotically, but according to intelligible laws. Substances were not fixed: they could be transmuted. Metals, in particular, were seen not as immutable elements but as stages in a developmental hierarchy, from base to noble, lead to gold. The logic was not unlike that of Aristotelian biology, which understood natural beings as striving toward a perfected form[13].

Alchemical theory in this period revolved around two key principles: the existence of a "prime matter" (*prima materia*) and the use of a "philosopher's stone" or *elixir* capable of achieving transmutation. These were not metaphors, though they carried allegorical weight. The *prima materia* was postulated as the undifferentiated substrate of all things, invisible and inert until shaped by form. The elixir, on the other hand, was the agent of transformation—sometimes conceived as a tincture, other times as a red powder or a liquid distillate—that could accelerate or complete nature's work. The alchemist's role, in this view, was to assist nature by providing the right conditions: the correct sequence of purification, the appropriate regimen of heat, the proper timing. It was, in many ways, a practice of care—a chemistry of patience rather than force[14].

One cannot overstate the technical sophistication of many of these operations. The pseudo-Geberian corpus, in particular, outlines methods for distillation, sublimation, calcination, and crystallization, describing apparatuses that include cucurbits, aludels, and alembics—tools that would remain in use for centuries. These texts employ language that is sometimes symbolic but often precise, offering recipes and protocols that suggest actual laboratory experience. They discuss the corrosive power of *aqua fortis* (nitric acid), the dissolution of gold in *aqua regia*, the handling of mercury and sulfur, and the preparation of what we would now call mineral acids—processes that would later be central to modern inorganic chemistry[15].

What is striking is that none of this was conceived as in opposition to theoretical thought. On the contrary, alchemy was deeply philosophical. Scholars like Roger Bacon and Arnald of Villanova saw it as an extension of natural philosophy, one that could uncover the "hidden properties" of matter—those not accessible to syllogism alone. The scholastic distinction between *manifest* and *occult* qualities did not render the latter irrational; it simply acknowledged that not all causality was reducible to immediate sense perception or deduction. In this space of the hidden, chemistry began to take shape—not as a modern discipline, but as a rational art concerned with change, proportion, and material interaction.

The moral and spiritual dimensions of this practice were not superficial additions. In many treatises, particularly those of the so-called *spiritual alchemists*, material purification was inseparable from ethical discipline. The alchemist's body had to mirror the purity of his operations. He was to abstain from greed, vanity, and impatience—vices thought to distort both the matter under treatment and the practitioner's own perception of nature's truth. The notion that the philosopher's stone could only be made by someone who had first transmuted his own soul was not metaphorical: it was methodological. Purity of work required purity of will[16].

This is perhaps the clearest point of divergence from modern chemistry. Where modern laboratories aim for objectivity and repeatability, medieval alchemy was self-reflective, even confessional. And yet, within this ethos, there emerged an empirical attention to detail that is unmistakable. Alchemists described colors, textures, fumes; they recorded reactions, failures, yields. Their works, though written in opaque and often deliberately cryptic language, preserved observations that later chemists would find intelligible and useful. In some cases, alchemical texts were reinterpreted in the seventeenth century as repositories of forgotten or disguised technical knowledge.

To dismiss these practices because they did not conform to modern expectations is to miss their historical role. Alchemy was not the primitive cousin of chemistry; it was its crucible. Its goals were often spiritual, its language symbolic, but its attention to the material processes was acute. If modern science stripped away the metaphysics and the soteriology, it did so after inheriting a corpus of methods, tools, and empirical insights that alchemy had painstakingly assembled. The transformation of matter, in the end, was never just about gold. It was about nature's potential, and humanity's responsibility to understand—and possibly, in some small way, to complete—it[17].

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[13] William R. Newman, *The Summa Perfectionis of Pseudo-Geber*, Brill, Leiden, 1991.

[14] Lawrence M. Principe, *The Secrets of Alchemy*, University of Chicago Press, 2013.

[15] William R. Newman, *Atoms and Alchemy*, University of Chicago Press, 2006.

[16] Stanton J. Linden, *The Alchemy Reader*, Cambridge University Press, 2003.

[17] For an overview of the topic of alchemy, see Martelli Matteo, *L'alchimista antico: dall'Egitto greco-romano a Bisanzio*, Editrice Bibliografica, Milano, 2019.

CHAPTER 4: ASTROLOGY, COSMOLOGY, AND THE PERMEABLE BORDERS OF SCIENCE

The medieval world did not categorize knowledge in the ways we do. The disciplinary boundaries that today separate chemistry from astrology, physics from cosmology, or even theology from natural science were, in the thirteenth and fourteenth centuries, far more fluid—porous, even deliberately so. Studying the stars was not to escape the material world but to understand its patterns. To practice alchemy was not to abandon reason, but to follow nature more deeply, perhaps into its invisible or occult dimensions. The assumption that underpinned much of this intellectual culture was that all things were connected: macrocosm to microcosm, celestial to terrestrial, soul to element. The cosmos was ordered, readable, and meaningful, and it was the task of the philosopher-scientist—not yet a separate figure—to decipher it.

Astrology, in this context, is a science of correspondences. It claimed that the configurations of heavenly bodies influenced, or reflected, events on earth—not deterministically, but with a logic of affinity. The moon affected tides; Mars, associated with heat and dryness, was thought to influence fevers and temperaments. This was not seen as magical thinking, but as part of the causal framework of the natural world. Thomas Aquinas himself allowed for a certain influence of the stars on human passions, though not on free will—an important distinction that placed astrology within the orbit of natural causality, not heretical fatalism[18]. Medical astrology became a standard part of practice: natal charts were used to diagnose imbalances of the humors, to time bloodletting or childbirth. These applications, now marginalized or dismissed, were integrated into university medicine from Montpellier to Padua[19].

What interests us here is not whether astrology was "true" by modern standards, but how it functioned intellectually. Like alchemy, astrology operates with a balance of theory and observation. Astronomical ephemerides were compiled with real attention to precision. Instruments such as the astrolabe were calibrated, annotated, and taught in schools. The boundary between astronomy (considered a mathematical science) and astrology (a practical application of celestial patterns) was acknowledged, but rarely absolute. Ptolemy's *Tetrabiblos*, transmitted through Arabic commentary, was one of the core texts that shaped medieval astrological theory—not as superstition, but as a rational system of probabilistic causation[20].

The same desire to trace hidden affinities animated the practice of natural magic—a term that included everything from herbology to the crafting of talismans. This, too, was often adjacent to alchemy. Both relied on the idea that substances contained *occult virtues*—not in the sense of being supernatural, but of having properties not immediately perceptible. The doctrine of "signatures"—that plants or minerals bore marks indicating their uses—was widely accepted. A yellow flower, for example, might treat jaundice; red stones might aid in blood disorders. These were not irrational deductions, but part of a wider epistemology that read nature as a symbolic text[21].

Alchemy thrived in this environment. It borrowed language from astrology, geometry, medicine, and theology—rarely feeling the need to choose between them. The operations of fire, condensation, fermentation, and sublimation were timed according to planetary hours. Recipes were framed by numerology and esoteric cosmology. Sulfur, for instance, was associated not only with combustibility but with Mars, masculinity, dryness, and action. These symbolic mappings did not replace empirical observation—they framed it. The act of refining mercury was both a physical procedure and a cosmological gesture, situated within a worldview that saw all matter as participating in a divine architecture[22].

This fluid epistemic space also helps explain why thinkers like Raimundus Lullus or Marsilio Ficino moved so easily between theology and natural philosophy. Ficino's translations of Hermetic texts, for instance, helped shape Renaissance alchemical and astrological thought by asserting a divine continuity between mind, cosmos, and substance[23]. The medieval origins of this hermeticizing trend lie earlier, however, in the fertile synthesis of Aristotelianism, Neoplatonism, and Arabic cosmology that had taken root in the Latin West by the late 1200s. Alchemy, in this light, becomes less an outlier than a crystallization of medieval science's deepest instincts: to unify, to symbolize, to transform.

Indeed, the anxiety that eventually grew around these disciplines—especially in the fifteenth and sixteenth centuries—was not because they had failed to

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[18] Thomas Aquinas, *Summa Theologiae*, I.115.4.

[19] Pearl Kibre, *Hippocrates Latinus: Receptions of Astrology in Medieval Medical Education*, Variorum, London, 1985.

[20] Jim Tester, *A History of Western Astrology*, Boydell Press, Woodbridge, 1987.

[21] Allen G. Debus, *Man and Nature in the Renaissance*, Cambridge University Press, 1978.

[22] Lawrence M. Principe and Newman, *Alchemy Tried in the Fire*, Princeton University Press, 2002.

[23] Michela Pereira, *Lullian Alchemy: Aspects and Problems of the corpus of Alchemical Works Attributed to Ramon Llull*, Catalan Review, 1990, Vol. IV, 1-2: 41-54.

produce results, but because they challenged emergent categories of orthodoxy. Alchemy promised transformation of matter and soul; astrology suggested knowledge of the future; both implied that nature was knowable in ways that threatened institutional control. It is no coincidence that these sciences became increasingly suspect at the very moment that natural philosophy was being formalized into the early modern “scientific” model. In that transition, we do not witness the birth of science ex nihilo, but the narrowing of what would count as scientific.

In the Middle Ages, the borders were not so fixed. Alchemy and astrology did not simply exist alongside natural philosophy—they were constitutive of it. The idea that knowledge required both *ratio* and *experientia* was common currency. One could observe a color change in a vessel, then interpret it astrologically, then explain it using Aristotelian qualities, then contemplate it as a reflection of divine order. This was not incoherence; it was integration. And for all the differences that separate their world from ours, that integrative ambition may be one of the most sophisticated—and least understood—legacies of medieval science.

CONCLUSION

To understand medieval science is not to measure it against modern standards, but to enter a different world of thought—one in which nature was saturated with meaning, and knowledge was inseparable from metaphysical, theological, and even moral concerns. It is tempting to treat the Middle Ages as a preparatory phase in the rise of scientific modernity, to isolate in hindsight the methods, theories, or tools that appear to anticipate Galileo, Boyle, or Lavoisier. But this kind of selective genealogy distorts more than it reveals. What matters more is how medieval thinkers conceived of inquiry itself: not as a mechanical extraction of facts, but as a form of participation in an intelligible cosmos, where observation, reasoning, and symbolic resonance were all seen as valid paths toward understanding.

This is especially evident in the alchemical tradition, which deserves far more than condescension or curiosity. Alchemy was not a failed science, nor merely a proto-science. It was, in its own time, a coherent and ambitious attempt to theorize and manipulate the material world, grounded in both philosophical speculation and hands-on experimentation. The fact that it operated within a symbolic register—drawing on astrology, cosmology, and soteriology—did not undermine its empirical insights. On the contrary, that symbolic dimension expanded the conceptual vocabulary available to its practitioners. If modern chemistry grew out of alchemy, it did so not by purging all that was unscientific, but by slowly disembedding itself from a different set of epistemological and spiritual commitments.

The institutions of medieval science—monasteries, universities, apothecaries’ workshops—enabled not only the preservation of classical knowledge but its transformation[24]. Figures like Albertus Magnus, Roger Bacon, and the anonymous authors of alchemical treatises did not merely comment on Aristotle; they interrogated nature, manipulated matter, and speculated about causes in ways that would have been unthinkable just a century earlier. Their methods were uneven, their terminology unstable, their results sometimes opaque—but the intellectual ambition behind them was unmistakable.

And so, to speak of medieval science is to speak of a form of knowing that did not distinguish sharply between nature and spirit, cause and purpose, technique and transformation. It is to acknowledge a period in which science was still a branch of philosophy—and philosophy, in turn, was entangled with cosmology, morality, and theology. In this entanglement lay both its limitations and its richness. The modern separation of disciplines, for all its analytical power, has often obscured the ways in which earlier forms of science asked questions we are only beginning to ask again: How does knowledge relate to transformation? What does it mean to know something well enough to change it—ethically, materially, spiritually?

In that light, medieval science does not appear primitive or regressive, but differently configured. Its legacy is not merely the techniques it passed down, but the questions it dared to ask—and the conviction, still worth considering, that to understand nature is, at least in part, to be changed by it.

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[24] Sébastien Moureau, *Min al-Kīmiyā’ ad Alchimiam. The Transmission of Alchemy from the Arab-Muslim world to the Latin West in the Middle Ages* in *Micrologus 28. The Arabic Sciences in the Western World*, edited by Charles Burnett, Danielle Jacquart, and Agostino Paravicini Bagliani, pp. 87–141.

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Research Article

"Observations on the possible electromagnetic nature of nucleon interactions and pions" — historical manuscript from 1969 by B. W. Ninham and C. Pask

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Abstract. This manuscript presents an historical perspective prepared by Barry Ninham and Colin Pask in 1969 on the connection between quantum electrodynamics theory and nucleon interactions. A new theory of strong interactions based on electromagnetic considerations is proposed. Energy and force range magnitudes are correctly given. A new theory of the pion emerges and the pion mass and lifetime are calculated. No strong interaction coupling constant is required.

Keywords: Lifshitz Theory, Semi-Classical Electrodynamics, Dispersion Forces, Mesons, Pion Interactions

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A. HISTORICAL PREFACE BY BOSTRÖM AND PARSONS

The general understanding [1] of nuclear and particle physics indicates, relying for instance on first-principle-lattice Quantum Chromodynamics simulations (QCD), that the main features of nuclear forces arising from the quark and gluon degrees of freedom can be described by the well-known QCD theory. The long-range behaviour of the nuclear force appears to be consistent with the pion-exchange potential [1]. Considering that these lattice QCD simulations usually neglect quantum electrodynamical interactions, it is usually assumed that electrons, positrons, and photons can be ignored when describing the main features of nuclear forces at the energy scale of pion exchange. However, an original manuscript, written around 1969 by Prof. Emeritus Barry W. Ninham and Dr. Colin Pask (with minor edits during the following years), showed how mesons of a mass 220 times the electron mass could emerge from Casimir's original derivation of the forces between perfectly reflecting plates. They also derived the lifetime of the uncharged mesons. That was prompted by a conversation with Freeman Dyson who told Ninham that Feynman had believed there ought to be a connection between electromagnetic theory and nuclear interactions. This Feynman never found. Later, Ninham and co-workers explored these links [2–5]. The force described by the Casimir effect [6] is related to the ideas developed by Ninham and Pask. In general van der Waals, Casimir, and Lifshitz interactions can be linked to boundary conditions of the electromagnetic field at the interface between two uncharged or charged surfaces [6–12]. These forces, in particular, have been measured [13–17], and recently for example predicted to impact the growth of ice at water-solid interfaces on planets, moons and exoplanets [18–20]. Remarkably, they also act between protons and neutrons on the nuclear scale [21]. The interpretations presented in the work by Ninham and Pask may perhaps be considered controversial by some, as they indicate that certain aspects of the well-established quantum field theories in nuclear and particle physics can be described using a semi-classical electrodynamical theory. Ninham and Mahanty went on to develop a semiclassical theory of molecular dispersion forces [22, 23], capable of describing the Lamb shift [24], and at the heart of which lay the molecular polarisability. The Ninham-Pask theory of pion interactions presented here could be extended to the case of uncharged neutrons by replacing the Klein-Gordon equation of eq.(2) with Mahanty and Ninham's semi-classical electromagnetic vector equation, and introducing the neutron polarisability [25–27] arising from charged quark interactions [28], related to the fine structure constant [29].

We are finally able to present the original work by Ninham and Pask in this historical contribution. The following foreward originates from an interview with Ninham by Boström and Parsons (only slightly edited). The authors of the preface and foreword take no credit for the science in the main section of this manuscript, which we consider to be of historical interest. We present this hidden treasure ahead of Barry Ninham's 90th birthday (9 April 2026). The historical manuscript starts from Section I, "Introduction".

B. FOREWORD FROM INTERVIEW WITH BARRY NINHAM

Barry Ninham wrote this previously unpublished paper after returning to Australia from USA in 1969. He has been then working with Adrian Parsegian at NIH working on Lifshitz theory, which few at the time could properly understand. At that time Ninham invited Colin Pask to be a coauthor. At this time Colin Pask was a young researcher working on nuclear physics – which was what the manuscript was about. After 55 years, Barry Ninham can not fully remember the background as to why this manuscript remained unpublished. Most likely Pask considered it too controversial, and pulled out. This is an all too common response, people are often afraid of anything out of the ordinary or new. At that time it was thought that there was no way electromagnetic theory could have anything to do with nuclear forces. Thus Ninham got discouraged and dropped it. Colin Pask had a long career and later wrote a magnificent biography of Newton who went to the same school in Lincolnshire as Pask. It is called *Magnificent Principia* [30]. Notably, Colin Pask was the first appointment Barry Ninham made when he took up his chair at Australian National University in 1971.

The concept of a quantum electrodynamic theory of nuclear interactions was later developed by Ninham and Boström [3, 4], though without calculation of lifetimes, following from on Ninham's earlier theoretical calculation of plasmon lifetimes, a substantial work confirmed experimentally by Powell and Swanson [31]. Lifetime calculations of muons were addressed more recently in an article by Ninham, Brevik and Boström in Substantia. [5]

As Barry Ninham, Adrian Parsegian, and George Weiss [9] showed in 1970, one can derive Lifshitz inter- actions across an intervening medium from semi-classical theory. It was supposed, along with the Lamb shift, to represent the pinnacle and confirmation of quantum electrodynamics – within the assumption about bulk medium up to a molecular distance from an interface. But how could it be derived from semi-classical theory? What was going on? What was going on was a sleight of hand whereby at a certain point in the formalism of Lifshitz theory, more correctly identifed as the DLP theory of Dzyaloshinskii, Lifshitz and Pitaevskii [7], one had to solve a so-called Dyson nonlinear integral equation for the dielectric susceptibility involving a coupling constant integral. DLP linearised this, rendering the whole thing analytical—and collapsing it to semi-classical theory, not the full QED embodied in the integral equation. So then it becomes interesting. Because IF the semi-classical theory is shown to be equivalent to the theory of weak interactions in particle physics, then we must conclude, or at least suspect, that particle physics theory is equally deficient. The particle physics theory is similarly built on a linear foundation, and is potentially equally flawed. If one dismisses the equivalence, then one has to ask where on earth this energy from the foundations of quantum electrodynamics went to. The problem is too profound to be dismissed.

Philosophically, we know—after Dyson's paper on Feynman's derivation of Maxwell's equations—that only causality and the finite velocity of light are involved, and the imposition of Planck quantisation is all that is required. We can seek further illumination by including magnetic susceptibility and bringing in developments in non-linear optics. Clearly there is much work still to do. Ironically, the linearisation of the coupling constant integration led to an early version of DLVO theory [32]. This was published by Sam Levine [33, 34]. The correct theory was done by Derjaguin with Landau in Russia in 1941 [35] and by Overbeek [36] working at Philips industries in occupied Holland during the war, protected by Verwey. Prior to his landmark 1941 paper with Landau, Derjaguin had already commented that Levine's error was a mishandling of the thermodynamic independence of ion charge from ion density profiles [37]. Levine stubbornly resisted correction, asserting the error was Derjaguin's (and Langmuir's) [38], although he started to acknowledge the need for a broader thermodynamic perspective during a wartime Faraday meeting of the Royal Society of Chemistry [39]. Levine's stubbornness was not well received by Derjaguin and Landau, who caustically referred to Levine's stance as a missed opportunity made "who knows why?" [40] (the English translation [41] does not fully convey the frustration emoted in the original text). It took Overbeek's private communications to convince Levine that the term he had missed was the ln *c* entropy of the ion density profile [42] (or osmotic energy [43]). It is rather ironic that Landau totally dismissed Levine's work because a linearisation assumption, which is to say, a mistake, was used by Dzyaloshinskii, Lifshitz and Pitaevskii in their general theory of van der Waals forces [44]. Levine learnt his lesson well, correcting Babchin's linearisation error [45] three decades later on the theory of electrostriction [46], albeit without acknowledging Derjaguin's equivalent criticism on the same question [47]. It is the same problem in classical statistical mechanics solving the Ornstein-Zernicke equations connecting the indirect and direct correlation functions, with a linear coupling constant coupling polarisation and density fluctuations in the OZ Hamiltonian [48]. In this case a sufficiently large coupling leads to divergent oscillatory nonlocal electrostatics, requiring additional coupling terms to regularise energies [49].

In accordance with Substantia's purview to promote the history of science, we present the work "Observations on the possible electromagnetic nature of nucleon interactions and pions" by Barry Ninham and Colin Pask, as a subject of historical interest. The original text commences here.

OBSERVATIONS ON THE POSSIBLE ELECTROMAGNETIC NATURE OF NUCLEON INTERACTIONS AND PIONS

BARRY NINHAM AND COLIN PASK, 1969

I. INTRODUCTION

At the present time there is much interest, both theoretical and experimental, in the theory of nucleons and related particle. It is not our intention to survey this field in detail. For example of recent papers see Ratner et al. [50] and Amaldi et al. [51]. Survey-discussion articles by Lee [52] and Drell [53] could be consulted, while the article by Kendall and Panofsky [54] is a non-technical survey. This is just a further step in the process which began with the explanation of the structure and properties of macroscopic systems in terms of molecules and atoms, continued with the theory of atoms as collections of electrons and nuclei, and then scaled down even further to the description of nuclear phenomena as manifestations of the existence and behaviour of nucleons. Recent high-energy experiments, particularly those using the SLAC electron beam, are now forcing theorists to regard nucleons as extended objects, and to reevaluate the old meson cloud model [55] or to look for new models. The constituents of the required new model are as yet unknown, but Feynman's generic term "parton" is widely used.

To the physicist (as against the mathematician or mathematical physicist) a theory of the structure and interaction of particles seems to be long overdue. Without an underlying model the work of recent years has become more and more mathematical, with the express aim of using as few of the most general physical principles as possible. Such principles might be relativistic invariance, causality and known conservation laws, giving rise to dispersion relations and unitary symmetry for example. The theory of quarks offered some hope, for as Weisskopf [56] has written: " . . . it serves as a simply describable realization of SU(3) symmetry. The latter is what remains of the quark model, if one removes the quarks - the grin of the Cheshire cat". Quarks may be partons, but their existence is as yet uncertain.

In this paper we do not consider the detailed nature of nucleon structure, but speculate on how that structure may enable electromagnetic theory to be built into strong and weak interaction theories as a major and unifying concept. (We note that current algebra strongly suggests such a close link, based however on plausible mathematics rather than on an underlying physical model. See Weisskopf [56], for example.)

In one sense we are suggesting that before postulating new mechanisms such as parton-parton forces, the known forces should be tried first. We do not exclude new types of forces which may also be of importance in explaining certain problems. A similar (but not analogous) situation occurs in alpha particle scattering: at low energies the α-α force will be electromagnetic, while the α particles themselves are held together by other forces. These other forces become of importance in the high energy – small distance region. In atom-atom interactions, on the other hand, the interaction and structure forces both have the same origin.

As a further general point we remark that we continue to use the usual quantum mechanics even in the subnucleon limit. The validity of this assumption is of course unknown, but quantum electrodynamics does appear to work at very small distances.

In section II we discuss the possibility of electromagnetic fluctuation forces being responsible for strong interactions. We assume further that at the very high photon frequencies involved there is an equilibrium between the photons and electron positron pairs as discussed by Landau and Lifshitz [57]. This introduces a plasma into our theory. Collective excitations may be set up in the plasma and we identify these plasmons with the pions of conventional theory. Such a theory enables the π^0 mass and lifetime to be calculated without introducing conventional strong or weak interaction theories. The details of this theory of the pion are presented in section III. Concluding remarks are made in section IV.

II. ELECTROMAGNETIC THEORY AND NUCLEON INTERACTIONS

The theory of electromagnetic fluctuation forces acting between macroscopic bodies is by now well established and understood [58], and is now being used at the microscopic level by McLachlan [59], Ninham and Parsegian [60, 61] and others. Fluctuation forces are of short-range and may be large, and so may be suitable candidates for explaining nuclear forces. In this paper we assume that the nucleons have structure which produces electromagnetic fluctuation forces, and, as a first step, we give some rough energy and distance arguments.

Consider two semi-infinite planes of nuclear material a distance d apart. If we consider perfectly reflecting planes, the electromagnetic energy of interaction per unit area due to the wave system set up in the gap as obtained by Casimir [6] (see also Power [62]) is

$$E_A = -\frac{\pi^2}{720}\frac{\hbar c}{d^3} \tag{1}$$

Now consider two protons with their centres d apart. As a first crude approximation, we use the above result with surface area πr_0^2, r_0 = proton radius ~ 0.9*f*. Then the attractive force is ~ $-[\pi 3\hbar c r_0^2]/[240\, d^4]$. A typical nuclear distance might be obtained by balancing this force with the repulsive Coulomb force $e^2/\ (2r_0 + d)^2$. This gives d ~ 5*f* with a corresponding energy 1/5MeV. Obviously one cannot expect too much from such a crude argument, but we feel that the important point is that the distance is of order fermis rather than Ångstroms or cm's., and the energy is of order MeV rather than ev or ergs. Somewhat more striking is the observation that the attractive electromagnetic energy between two nucleons at a distance of 1f as computed by the above procedure is ≈ 10MeV!

To proceed further we would need to assume or deduce details of the nucleon structure, i.e. the electromagnetic susceptibility.

III. ELECTROMAGNETIC THEORY AND PIONS

In the standard scalar theory, nuclear interactions proceed via a field described by the Klein-Gordon equation, which in Fourier space may be cast into the form

$$\nabla^2\varphi_\omega - \frac{\omega^2}{c^2}\left(1 - \frac{\mu^2 c^2}{\omega^2}\right)\phi_\omega = 0 \tag{2}$$

where $\mu = m_\pi c/\hbar, m_\pi$ = pion mass. There is a suggestive similarity between this equation and that for the Maxwell scalar potential. In the high frequency regime we therefore identify $1 - (\mu^2 c^2)/\omega^2$ with the electromagnetic susceptibility ε(ω) which here has the form appropriate to a plasma.

Thus we obtain where

$$\mu^2 c^2 = \omega_\rho^2 = \frac{4\pi N e^2}{m_e} \tag{3}$$

m_e = electron mass, and N the electron number density. (The standard plasma theory considers a set of negative charges with a smeared-out positive background to preserve electrical neutrality. Here the positive component of our system is the positron gas and we should actually use a theory of an electron-positron plasma. However no such theory is available in detail, and we believe the conventional theory can be used in any first rough studies).

Eq. (3) contains m_π and N which are still unknown. We now give arguments which determine these and other important quantities.

Mass of the pion

Again we consider the nuclear material slabs interacting across a gap of width d. The electromagnetic energy in the gap has a density E which follows from Eq. (1):

$$\mathrm{E} = -\frac{\pi^2}{720}\frac{\hbar c}{\mathrm{d}^4} \tag{4}$$

The equivalent temperature of this (virtual) energy can be found by saying that the energy involved is the same as a unit volume black box,

$$\mathrm{E} = \frac{\pi^2 (\mathrm{kT})^4}{15(\hbar c)^3} \tag{5}$$

Thus we obtain,

$$\mathrm{kT} = \frac{\hbar c}{2 \times 3^{1/4}\mathrm{d}}. \tag{6}$$

Actually, we will have a system of photons plus electronpositron pairs. If we assume d ~ 1f the equivalent temperature is so high, kT ~ 140 m_ec^2 and the black box will contain almost the maximum number of e^+e^- pairs. We then obtain [57]

$$\mathrm{N} = \mathrm{N}^- \approx 0.183 \times \left(\frac{\mathrm{kT}}{\hbar c}\right)^3 \tag{7}$$

We now take d ~ 1 fm, calculate N using Eqs. (6) and (7) and hence obtain the pion mass using Eq.(3). This gives

$$\mathrm{m}_\pi \approx 220 \ \ \mathrm{m}_\mathrm{e} \tag{8}$$

which compares favourably with the experimental result $m_\pi \simeq 270\ m_e$.

The neutral pion lifetime

The pion plays a key role in the usual theory of nuclear forces, e.g. Wick [63] used its mass to predict the force range. We have already shown how range, energy considerations and the pion mass are connected in our theory. We can now proceed to a further property of the pion by using our assumption that the collective excitations in the plasma produced by the electromagnetic fluctuations are to be identified with pions. This is simplest for π^0. Now although plasma theory is at present far from complete, we believe that the plasma lifetime calculations given by Ninham [64] should give a correct order of magnitude for the present case. The lifetime mentioned is for the decay plasmon → two e^+e^- pairs. In the sea of e^+e^- pairs, these can decay into photons. Using Eq. (10) given by Ninham [64], with q associated with $m_\pi c^2$, we obtain

$$\pi^0 \ \ \text{lifetime} \leq 1.5 \times 10^{-17}\text{s}. \tag{9}$$

The current experimental value is (0.84 ± 0.1)´10^{-16} s [65]. Clearly this theory predicts various decay modes for π^0, all in terms of e^+e^- pairs and photons, again in agreement with experiment. The coupling of the neutral pion to the electromagnetic field raises no problems in this theory. In the older conventional theory an intermediate proton-anti-proton state is introduced, $\pi^0 \to p\bar{p} \to 2\gamma$ [66], and thus the coupling is via strong interactions. The π^0 lifetime may then be related to proton Compton-scattering as in Jacobs and Mathews [67]. More recent theories seem unable to account for π^0 decay and it remains one of the three "unresolved" problems of current algebra, according to Beg [68]. We note that our result does not involve relations with other processes and does not contain any strong interaction coupling constant.

Plasmon critical wavenumber

There is a critical wave number k_c for plasmon existence [69]. Clearly, this is related to the interaction energy of nucleons and pion energies and masses in this theory. However, the theory for k_c is still uncertain, and so, at this stage, we do not attempt to use this effect in any detail.

IV. CONCLUSIONS

We do not claim any great accuracy for the above calculations, but rather, we take the point of view that our rough ideas could lead to an interesting quantitative theory if correctly interpreted. For example, the plasma theory for the pairs and densities we postulate would need to be investigated.

As regards the description of particles other than π^0, several possibilities may be considered. Associating charge with a plasmon could give $\pi^{\pm}$. Decay of charged pions could reveal the role of the muon in particle theory, and of course, this would then bring weak interactions into the theory. One could also consider a generalized vector Klein-Gordon equation with a "magnetic susceptibility" term in analogy with the electromagnetic vector potential equation.

Finally, we point out that we consider basically nuclear interactions and not "free particles in a vacuum" since any "observed vacuum" is always bounded by interacting matter. (However, we note that all electron theories from Dirac's negative energy states sea onwards have contained vacuum fluctuations. Hence, a sea of (virtual) $e^{+}e^{-}$ pairs (as in our theory) is associated even with the vacuum). Thus our ideas are in line with recent attempts to use only real particles and to avoid the difficulties associated with a description based on free, bare particles with interactions then introduced via perturbation theory.

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Figure 1: Graphical Abstract: Barry Ninham, founder of the Department of Applied Mathematics at the Australian National University in 1970.

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Research Article

Paramagnetic Contrast Agents in MRI: A Review

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Abstract. Magnetic Resonance Imaging (MRI) is a powerful, non-invasive imaging technique widely used in medical diagnostics. However, its inherent inability to differentiate between certain tissues can limit its diagnostic capabilities, especially when distinguishing between subtle tissue differences. To overcome these limitations, contrast agents are employed to enhance the images produced by MRI and improve the clarity and accuracy of the results. This review delves into the role, types, and advancements of paramagnetic contrast agents in MRI.

Keywords: MRI, Contrast Agents, Paramagnetic

1. PARAMAGNETISM

Paramagnetism refers to the magnetic behavior of substances that are attracted to an external magnetic field due to the presence of one or more unpaired electrons in their atomic or molecular orbitals. These unpaired electrons possess intrinsic magnetic moments (spin angular momentum), which interact with external magnetic fields, resulting in a net magnetic moment. Unlike diamagnetic materials, which are repelled by a magnetic field due to paired electrons and a negative magnetic susceptibility, paramagnetic materials exhibit a positive magnetic susceptibility, though typically small and only observable in strong magnetic fields (1).

The magnitude of paramagnetism in a substance depends on the number of unpaired electrons and their spatial distribution. According to Curie's Law, the magnetic susceptibility of paramagnetic materials is inversely proportional to temperature (2). This relationship reflects the thermal agitation that disrupts the alignment of magnetic moments at higher temperatures, reducing net magnetization.

Common examples of paramagnetic substances include transition metal ions such as $Fe^{2+/3+}$, $Mn^{2+/3+}$, and Cu^{2+}, as well as molecular oxygen (O_2) in its ground triplet state. In solid-state physics and chemistry, paramagnetism is frequently analyzed through techniques such as electron paramagnetic resonance (EPR), which detects the energy transitions of unpaired electrons in a magnetic field (3).

Paramagnetism is a quantum mechanical phenomenon fundamentally rooted in the Pauli exclusion principle and Hund's rules, which govern the occupancy of electron orbitals in atoms and molecules. The presence of unpaired electrons creates localized magnetic dipoles that, although randomly oriented in the absence of a magnetic field, tend to align parallel to an applied field, generating a weak attraction.

2. INTRODUCTION TO MRI CONTRAST AGENTS

Magnetic Resonance Imaging (MRI) contrast agents (CAs) are specialized compounds administered to patients—usually intravenously—to enhance the visibility of internal anatomical structures and pathological conditions during MRI scans. These agents work by altering the relaxation times (T_1 and T_2) of nearby hydrogen nuclei (protons), thus modifying the intensity of the MRI signal in affected regions. The result is improved signal contrast between different tissues, which helps distinguish normal anatomy from abnormalities such as tumors, inflammation, vascular malformations, or ischemia (4,5).

Contrast agents primarily fall into two categories: T_1-weighted (positive) agents, which shorten the longitudinal relaxation time and appear bright on T_1-weighted images, and T_2-weighted (negative) agents, which shorten the transverse relaxation time and appear dark on T_2-weighted images (6). The most widely used MRI contrast agents are based on gadolinium (Gd^{3+}), a paramagnetic lanthanide ion with seven unpaired electrons that significantly enhances the T_1 relaxation rate of surrounding water protons. Because free gadolinium is highly toxic, it is administered as a chelated complex (e.g., Gd-DTPA or Gd-DOTA), which safely sequesters the metal ion while retaining its magnetic efficacy (7) (Figure 1).

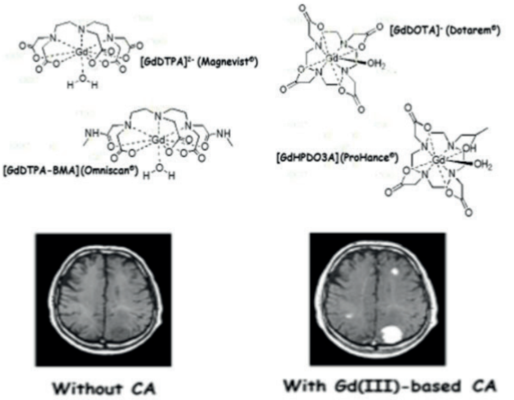

Figure 1. Chemical structures of Gd3+ complexes used in clinical practice. They yield a marked hyperintensity in the anatomical region where they distribute. The presence of tumour lesions is clearly highlighted thanks to the vascular leakeage of neo-formed vessels.

In addition to gadolinium-based contrast agents (GBCAs), iron oxide nanoparticles are used as T_2 agents, particularly in imaging the liver, spleen, and lymph nodes, due to their strong magnetic susceptibility and ability to induce signal loss in surrounding tissues (8). More recently, research has expanded into new classes, like the relaxation enhancing manganese(II)- and iron(III)-based agents, as well as systems exploiting heteronuclei such as fluorine-based agents (9). Furthermore, the field has been further widened by exploiting routes to change the MRI response based on the saturation of exchanging protons (10). Moreover much attention has been devoted to the design of smart (responsive) contrast agents, which are activated in specific physiological environments or in response to particular biomarkers (11).

Contrast-enhanced MRI plays a critical role in clinical diagnostics, enabling early detection and precise localization of lesions, vascular pathologies, and neurodegenerative conditions. However, safety concerns, especially regarding nephrogenic systemic fibrosis (NSF) associated with certain GBCAs in patients with renal impairment, have led to ongoing development of safer and more efficient agents (12,13).

3. MECHANISM OF ACTION OF PARAMAGNETIC MRI CONTRAST AGENTS

MRI contrast agents primarily function by modulating the behavior of water protons within biological tissues, thereby enhancing image contrast and improving diagnostic clarity. The underlying mechanism centers on the effect of contrast agents on proton relaxation times, particularly the longitudinal relaxation time (T_1) and the transverse relaxation time (T_2). These relaxation times govern how quickly protons return to their equilibrium states after being excited by the MRI's radiofrequency pulse. Contrast agents typically contain paramagnetic or superparamagnetic substances, which interact with the magnetic moments of nearby hydrogen nuclei (water protons), altering the local magnetic environment (4,5).

Paramagnetic contrast agents, such as those based on gadolinium (Gd^{3+}), contain unpaired electrons that create fluctuating local magnetic fields, which increase the efficiency of energy transfer between protons and their surroundings. This accelerates longitudinal (T_1) relaxation, leading to brighter signal intensities on T_1-weighted images—hence, these are often referred to as positive contrast agents (6,7). In contrast, superparamagnetic agents, such as iron oxide nanoparticles, generate strong microscopic magnetic gradients that accelerate transverse (T_2) relaxation, causing rapid dephasing of proton spins. This leads to signal loss and darker images on T_2-weighted sequences, classifying them as negative contrast agents (8).

The efficiency of a contrast agent in altering relaxation times is quantified by its relaxivity (r_1 and r_2), which reflects its capacity to enhance the relaxation rates ($1/T_1$ and $1/T_2$) per unit mM concentration. Relaxivity depends on several factors, including the molecular structure of the agent, the coordination geometry of the metal ion, the number and exchange lifetime of inner-sphere water molecules and rotational correlation time (4) (Figure 2). Additionally, the local tissue environment—such as pH, temperature, and the presence of macromolecules—can modulate the relaxivity and hence the contrast enhancement efficacy.

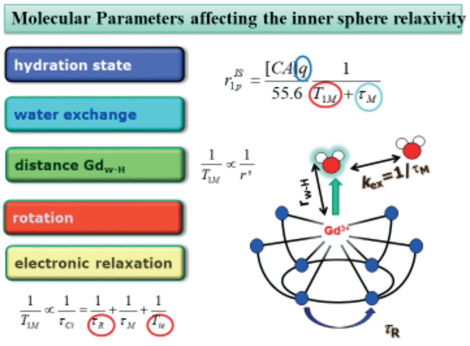

Figure 2. The performance of Gd-based MRI contrast agents has been improved by acting on their molecular structure and on their dynamics.

In clinical imaging, the choice of contrast agent and imaging sequence (T_1- or T_2-weighted) is tailored to the diagnostic objective, such as detecting tumors, assessing vascular integrity, or visualizing inflammatory processes. Advances in contrast agent development are increasingly focused on creating targeted or responsive agents that selectively accumulate in pathological tissues or change their magnetic properties in response to physiological triggers (11).

4. TYPES OF MRI CONTRAST AGENTS

MRI contrast agents are critical tools in enhancing the diagnostic capabilities of magnetic resonance imaging. They work primarily by altering the relaxation times of nearby hydrogen nuclei, thereby enhancing image contrast between different tissues. Among the broad classes of paramagnetic contrast agents used in clinical and experimental imaging, the most prominent include gadolinium (Gd)-, manganese (Mn)-, and iron (Fe)-based complexes, iron oxide nanoparticles, and paramagnetic chemical exchange saturation transfer (paraCEST) agents.

(i) Gadolinium-Based Contrast Agents (GBCAs)

Gadolinium-based contrast agents are the most widely used in clinical MRI. Gadolinium (Gd^{3+}), a lanthanide metal, possesses seven unpaired electrons, making it highly paramagnetic. This property allows GBCAs to significantly reduce the longitudinal relaxation time (T1) of nearby water protons, resulting in brighter signal intensities on T_1-weighted images. GBCAs are particularly valuable in imaging vascular structures, tumors, and regions with compromised blood-brain barrier integrity (14,15).

To mitigate gadolinium's inherent toxicity—as free Gd^{3+} ions are toxic due to their interference with calcium biochemistry—GBCAs are formulated as chelates, where the Gd^{3+} ion is tightly bound to organic ligands. These ligands are primarily classified as linear or macrocyclic, based on their chemical architecture.

- **Linear GBCAs**: These have an open-chain chelating structure. While they are effective at enhancing signal intensity, their kinetic stability is lower, which increases the risk of gadolinium dissociation, especially in patients with impaired renal function. Examples include gadodiamide and gadopentetate dimeglumine (16,17).
- **Macrocyclic GBCAs**: These agents encase the gadolinium ion in a rigid ring-like structure, providing greater thermodynamic stability and kinetic inertness. This arrangement significantly reduces the release of free Gd^{3+} ions, thereby lowering the risk of adverse effects such as nephrogenic systemic fibrosis (NSF). Widely used macrocyclic agents include gadobutrol, gadoterate meglumine, and gadoteridol (18,19). Recently Gadopiclenol (a system with two water molecules in the inner coordination sphere) has been introduced (20)
- Much work has been done to get an in-depth understanding of the structural, electronic and dynamic parameters that control the observed relaxivity of Gd-containing agents (21) (Figure 2).

(ii) Manganese (Mn)- and Iron (Fe)-Based Complexes

Manganese and iron are emerging as biocompatible alternatives to gadolinium due to their status as essential trace elements in the human body. Although these ions have fewer unpaired electrons (Mn^{2+} has 5; Fe^{3+} has 5), they are still paramagnetic and capable of T1 signal enhancement, especially when appropriately chelated or incorporated into nanoparticle structures.

- **Manganese-Based Agents**: Manganese, often used in the form of manganese chloride ($MnCl_2$) or chelates like Mn-DPDP (mangafodipir), enters cells via calcium channels and can serve as a surrogate biomarker for cellular viability or activity (22,23). Its use is being revisited in manganese-enhanced MRI (MEMRI), particularly in neuroscience and cardiology research. However, concerns about neurotoxicity at high doses have limited its widespread clinical use (24).
- **Iron-Based Complexes**: Iron-based MRI agents include ferric iron chelates and iron oxide nanoparticles. While superparamagnetic iron oxide nanoparticles (SPIONs) are more traditionally associated with T2-weighted imaging (discussed below), iron3+ chelates are being explored for their potential T1 contrast capabilities. These agents benefit from endogenous metabolic pathways for clearance and storage, reducing concerns about long-term deposition (24).

The use of Mn and Fe as alternatives to Gd is under intense scrutiny, especially in preclinical settings, due to their potential to offer safer, biodegradable options with low systemic toxicity, particularly important for vulnerable populations such as children, pregnant women, or patients requiring frequent imaging.

(iii) Metalloporphyrins:

Paramagnetism is often associated with the presence of metal ions at the center of the porphyrin ring. Metalloporphyrins are highly relevant due to their diverse roles in biological systems, such as in hemoglobin, cytochromes, and chlorophyll, and their use in various applications including catalysis and sensors. The metal center in a metalloporphyrin can significantly influence the electronic structure, which in turn impacts the magnetic properties of the compound. The metal ion can either contribute unpaired electrons to the system, inducing paramagnetism, or alter the electronic environment to promote coordination with ligands that can lead to distinct magnetic behaviors. For instance, iron (III)-containing metalloporphyrins (e.g., ferriprotoporphyrin IX) are typically paramagnetic due to the presence of unpaired electrons in the d-orbitals of the iron ion. Similarly, manganese (III) porphyrins exhibit paramagnetism due to the partially filled d-orbitals of manganese. The magnetic susceptibility of these systems can be influenced by factors such as the ligand field around the metal, spin-state splitting, and temperature, among others (25).

The paramagnetic behavior of metalloporphyrins is particularly useful for understanding their interactions with other molecules, such as in enzyme catalysis or electron transfer processes. For example, studies on the paramagnetism of cobalt (III) porphyrins have revealed insights into their role in oxidative catalysis and their ability to activate molecular oxygen (26). The understanding of the magnetic properties of these systems is not only crucial for biological systems but also for their potential application in materials science, The paramagnetic behavior of metalloporphyrins is particularly useful in the development of novel magnetic sensors or drug delivery systems. Additionally, their magnetic properties make them suitable candidates for use in magnetic resonance imaging (MRI) as contrast agents (27).

(iv) Iron Oxide-Based Contrast Agents

Iron oxide-based contrast agents, particularly superparamagnetic iron oxide nanoparticles (SPIONs) and ultrasmall superparamagnetic iron oxides (USPIOs), are an important class of negative contrast agents in MRI. These agents work by shortening the transverse relaxation time (T_2 or T_{2^*}), leading to a decrease in signal intensity (darkening) on T_2-weighted images. The core of these nanoparticles typically consists of magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3), surrounded by a biocompatible coating (e.g., dextran, PEG) to enhance stability and reduce immunogenicity (28,29).

SPIONs are especially effective in imaging the reticuloendothelial system (RES), including the liver, spleen, and lymph nodes, because macrophages rapidly phagocytose the particles. This allows for detection of lesions or tumors that do not take up the agent, appearing as hyperintense (bright) areas against a darkened background (30). Additionally, SPIONs have shown promise in cell tracking, magnetic drug delivery, and theranostic applications, owing to their ability to be functionalized with targeting ligands or drugs (31).

Despite their advantages, SPIONs have faced regulatory and commercial setbacks. For example, Feridex® and Resovist®, two clinically approved SPION agents, were withdrawn from the market due to limited clinical demand and high production costs, though a superparamagnetic iron oxide nanoparticle that has been approved in the United States, Europe, and Canada for intravenous iron supplementation research continues robustly in this area (32). Currently the off-label use of Ferumoxytol (a superparamagnetic iron oxide nanoparticle that has been approved in the United States, Europe, and Canada for intravenous iron supplementation) appears as an efficient replacement in these applications (33).

(v) Eu2+ Contrast Agents

Some attention has been devoted to Eu2+ based agents because the number of unpaired electrons in this ion is the same as the one of Gd3+ (i.e. 7 unpaired electrons). The most attractive application appears to look at them as reporters of the tissue oxygenation state as the transformation from Eu2+ to Eu3+ causes a marked reduction of the relaxivity being the latter almost "silent" as relaxation enhancer for water protons (34).

(vi) ParaCEST Contrast Agents.

Paramagnetic Chemical Exchange Saturation Transfer (paraCEST) agents represent a novel and versatile class of MRI contrast agents. Unlike tradition1al T_1 or T_2 agents that rely on altering relaxation times, paraCEST agents generate contrast through a frequency-selective saturation transfer mechanism. A radiofrequency (RF) pulse is applied at the resonance frequency of exchangeable protons saturating their magnetization. These saturated protons then exchange with bulk water protons, causing a reduction in the bulk water signal, which is detectable in the image (35).

One major advantage of paraCEST agents is that their contrast can be turned on or off "at will" by adjusting the RF pulse, allowing for tunable and multiplexed imaging—multiple agents can be selectively visualized based on their chemical shift. ParaCEST agents often incorporate lanthanide ions like Eu^{3+}, Tm^{3+}, or Yb^{3+}, which induce a large paramagnetic shift in the exchangeable proton resonance, enabling selective excitation and efficient contrast (36).

A leading figure in the development of paraCEST agents is A. Dean Sherry, whose pioneering work introduced the use of lanthanide-based DOTA-tetraamide complexes as responsive MRI contrast agents (37). His research demonstrated how paramagnetic ions could create large chemical shifts in exchangeable protons, facilitating the design of highly specific and tunable probes. Sherry's lab further developed molecular imaging agents responsive to biological variables such as pH (38), glucose (39), and metal ions like Zn^{2+} (40), significantly enhancing the functional imaging potential of MRI. He also contributed to the advancement of imaging methodologies such as frequency-labeled exchange transfer to improve in vivo detection of these agents (41).

An exciting development in this field is the creation of LipoCEST agents, which consist of liposomes encapsulating paramagnetic shift reagents within their aqueous cores. These systems confine the paraCEST agent, improving sensitivity and enabling compartmentalized contrast. LipoCEST agents are being explored for molecular and responsive imaging, such as detecting pH, enzyme activity, or temperature changes in localized tissue environments (42,43).

Furthermore, paraCEST agents are under active development for use as biosensors, particularly in cancer and neurological imaging, where they can provide functional information—such as changes in tumor microenvironment or enzyme expression—that goes beyond traditional anatomical imaging (44,45).

(vii) Effects of Paramagnetic Agents on the Endogenous MR-CEST contrast

CEST (Chemical Exchange Saturation Transfer) is an emerging modality in MRI. As anticipated above reporting on paraCEST agents, it relies on the transfer of saturated magnetization to the bulk water signal upon the RF irradiation of the absorption of mobile protons of a given solute in slow/intermediate exchange regime with water. In biological tissues, the exchangeable pool of protons is provided mostly by N-H and O-H functionalities on endogeneous proteins, creatine, free aminoacids and alcoholic groups. Basically, the endogenous CEST effect increases with the concentration of mobile protons and their exchange rate (still remaining in the slow/intermediate exchange regime) and decreases with the shortening of the water proton relaxation time. T_1 of water protons can be markedly decreased by the addition of paramagnetic agents.

It has been deemed of interest to exploit the effects of paramagnetic agents on the endogenous CEST response (46). The T_1 shortening causes a decrease of the Saturation Tranfer thus allowing to track phenomena reporting on the local biodistribution of the GBCAs and on the dynamics of the water molecules "labelled" by the interaction with the paramagnetic agent. Interestingly, since the endogenous CEST effect arises essentially from intracellular molecules, it follows that this experiment allows to map the differences in the permeability of cell membranes. The cycling of water molecules across the cell membrane reports about the activity of transporters that are overexpressed/up-regulated in tumor cells i.e. in turn on the cell metabolism (Figure 3). By applying this procedure one may generate maps reporting on the changes in water permeability of tumour cell membranes *via* the modulation of the endogenous (intracellular) CEST response by the decrease of water proton T_1 affected by the presence of a Gd-contrast agent in the extracellular space.

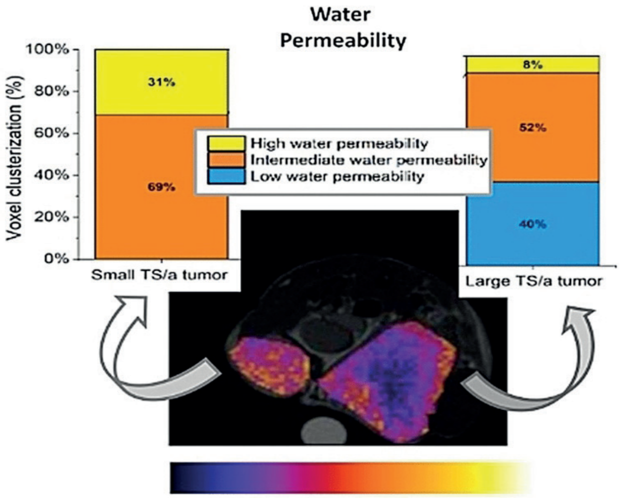

Figure 3. Map of the tumour regions reporting the changes of the endogenous CEST response upon the administration of a Gd-containing agent. The paramagnetic agent distributes in the extracellular space causing a shortening of T_1 of the water protons in this compartment. The transfer of these "labelled" water molecules to the intracellular compartment (where the endogenous CEST response is generated) causes a reduction of the CEST effect that is dependent on the differences in water permeability of the tumour cells. The heterogeneity in the distribution of voxels representing low, intermediate and high membrane permeability reflects changes in number and type of membrane transporters, i.e. a tool to get more insight into the differences in cell metabolism.

5. CLINICAL APPLICATIONS OF MRI CONTRAST AGENTS

MRI contrast agents—particularly gadolinium-based contrast agents (GBCAs)—play a pivotal role in enhancing diagnostic accuracy across multiple organ systems by improving tissue contrast and highlighting pathological changes. Their utility spans several major clinical domains:

- **Neuroimaging**: In brain imaging, GBCAs are essential for detecting and characterizing intracranial tumors, multiple sclerosis (MS) plaques, stroke, and infections. Under normal conditions, the blood-brain barrier (BBB) restricts the entry of contrast agents into the brain parenchyma. However, in areas of pathology where the BBB is disrupted—such as in gliomas or inflammatory lesions—contrast agents can accumulate, enhancing these regions on T_1-weighted MRI (47,48). This selective enhancement is critical for delineating lesion boundaries, assessing disease activity in MS, and guiding neurosurgical planning.
- **Oncology**: MRI contrast agents are widely employed in cancer diagnostics, staging, and treatment monitoring. Tumors typically exhibit increased vascular permeability and abnormal angiogenesis, allowing contrast agents to preferentially accumulate within malignant tissues—a phenomenon exploited in dynamic contrast-enhanced MRI (DCE-MRI) (49,50). This technique provides valuable information about tumor perfusion, vascular density, and response to therapy. GBCAs, as well as experimental agents like metalloporphyrins, have shown promise for targeting tumor-specific microenvironments and enhancing tumor-to-background contrast (11).

Paramagnetic metalloporphyrins have emerged as promising agents in cancer imaging and therapy due to their unique physicochemical properties and biological behavior. One of their most notable characteristics is their natural tendency to accumulate in tumor tissues, a phenomenon attributed to both the enhanced permeability and retention (EPR) effect and the specific affinity of porphyrin structures for cancerous cells (51,52). Leveraging this tumor-selective uptake, paramagnetic metalloporphyrins—such as those incorporating manganese or iron—have been investigated as magnetic resonance imaging (MRI) contrast agents. Studies have demonstrated their efficacy in enhancing the visibility of tumors in vivo, especially in preclinical models using human tumor xenografts in mice (53-56). These agents offer high relaxivity and favorable biodistribution profiles, with some formulations showing minimal aggregation or dimerization in aqueous environments, which further improves their imaging utility.

Recent advances have also explored the structural modification of metalloporphyrins to improve their pharmacokinetics and imaging specificity. For instance, conjugation with targeting ligands or incorporation into liposomes or nanoparticles can enhance their accumulation in tumor tissues and reduce off-target effects (57-59). Furthermore, dual-modality imaging using metalloporphyrin-based agents that combine MRI with fluorescence or positron emission tomography (PET) has been developed to provide complementary diagnostic information (60,61).

Beyond diagnostics, paramagnetic metalloporphyrins are gaining attention in therapeutic applications, particularly in the development of magnetically guided drug delivery systems. By attaching therapeutic agents to metalloporphyrin complexes, researchers have engineered multifunctional constructs that respond to external magnetic fields, thereby enhancing drug localization at tumor sites and minimizing systemic toxicity (62,63). This dual-function approach holds promise for integrating imaging and therapy—so-called theranostics—into a single platform. Moreover, the ongoing development of nanoparticle-based delivery systems incorporating metalloporphyrins is anticipated to further increase targeting specificity and therapeutic efficacy while reducing adverse side effects (64,65). These innovations represent a significant advancement in precision oncology, facilitating both the early detection and effective treatment of malignant tumors.

- **Cardiovascular Imaging**: MRI contrast agents are instrumental in evaluating myocardial perfusion, ischemia, and viability. In cardiac MRI, GBCAs help visualize coronary arteries, detect myocardial infarction, and assess fibrosis or scar tissue using late gadolinium enhancement (LGE) techniques (66). Additionally, contrast-enhanced MR angiography (CE-MRA) provides noninvasive visualization of vascular abnormalities such as aneurysms, stenoses, and congenital heart defects (67).
- **Musculoskeletal Imaging**: In musculoskeletal (MSK) applications, contrast agents enhance the detection of inflammatory, infectious, and neoplastic conditions. They are particularly useful in evaluating synovial inflammation in rheumatoid arthritis, soft tissue abscesses, osteomyelitis, and soft tissue tumors (68,69). Contrast-enhanced MRI can also differentiate between viable and necrotic tissue in cases of trauma or postoperative complications, aiding clinical decision-making.

These diverse clinical uses underscore the versatility of MRI contrast agents in modern diagnostic imaging. The continued development of novel contrast materials, including targeted, biodegradable, and theranostic agents, promises to expand their utility even further.

6. SAFETY AND RISKS

While MRI contrast agents—particularly gadolinium-based contrast agents (GBCAs)—are widely regarded as safe and well-tolerated in the general population, their use is not entirely without risk. Millions of doses are administered annually with a low incidence of acute adverse reactions, which are usually mild and include nausea, headache, dizziness, or injection site discomfort (70). However, more serious concerns have emerged, particularly in relation to renal impairment and gadolinium retention. In principle, also Mn2+ and Fe3+ based Contrast Agents too own some risk. For the former ones, the main concern deals with the in vivo release of manganese ions that may interfere with the homeostasis of this essential metal ion. For Fe+ based systems, main risks appear to be associated to the potential formation of OH radicals and ROS in the case water molecules enter its inner coordination sphere (Fenton reaction).

One of the most significant complications associated with GBCAs is nephrogenic systemic fibrosis (NSF), a rare but debilitating disorder that can occur in patients with severe renal dysfunction (glomerular filtration rate <30 mL/min/1.73 m^2). NSF is characterized by progressive fibrosis of the skin, joints, and internal organs, often leading to severe disability or death. The condition was first linked to gadolinium exposure in 2006 (71), and subsequent studies confirmed that certain linear, non-ionic GBCAs pose a higher risk due to their lower kinetic stability and greater likelihood of releasing free gadolinium ions (Gd^{3+}) in vivo (72,73).

In response, regulatory agencies such as the FDA and EMA issued safety guidelines restricting the use of high-risk GBCAs in at-risk populations, especially those with chronic kidney disease (CKD) or acute kidney injury. Today, macrocyclic GBCAs, which have a more stable and inert chemical structure, are preferred in clinical practice for their lower propensity to release gadolinium and their association with a significantly reduced risk of NSF (12,74);

A second area of concern involves the retention of gadolinium in brain tissues—notably in the dentate nucleus and globus pallidus—even in patients with normal renal function. This issue was first observed via increased T_1 signal intensity on non-contrast MRIs in patients who had received multiple doses of GBCAs (18). Follow-up studies confirmed that both linear and macrocyclic agents could lead to gadolinium deposition, although the extent and persistence appear to be greater with linear agents (75,76). While no clinical consequences have yet been established to date, the long-term effects of gadolinium accumulation remain under intense scrutiny, prompting precautionary approaches in pediatric, pregnant, and repeat-scan populations.

To cope with these concerns, contrast agents manufacturing companies have recently introduced Gd-based contrast agents endowed with higher relaxivities that provide the same diagnostic response of the first generation systems at markedly lower administration doses.

Moreover, hypersensitivity reactions, although rare, have been reported. These include mild allergic responses and very infrequent anaphylactic reactions, with incidence rates estimated between 0.01% and 0.1% (77). Informed consent, appropriate screening for renal function (typically via eGFR), and risk-benefit evaluation remain essential components of safe GBCA administration.

Continued research is underway to develop non-gadolinium-based contrast agents and biodegradable nanoparticles, aiming to reduce safety risks while preserving diagnostic efficacy (78). Such advances may further improve the safety profile of MRI contrast agents in the future.

7. RECENT ADVANCES IN MRI CONTRAST AGENTS

In recent years, research into MRI contrast agents has shifted toward the development of next-generation agents that not only enhance imaging quality but also improve safety profiles, enable molecular targeting, and even combine diagnostic and therapeutic functions. These innovations aim to overcome the limitations of conventional gadolinium-based contrast agents (GBCAs), particularly concerns related to gadolinium deposition and non-specific tissue enhancement, while enhancing the ability to visualize complex biological processes at the molecular and cellular levels.

- **Targeted Contrast Agents**: A major frontier in MRI contrast development involves the creation of target-specific agents that can recognize and bind to biomolecular markers associated with particular diseases, such as cancer, inflammation, or neurodegeneration. These agents are typically conjugated with ligands—such as antibodies, peptides, or small molecules—that bind to overexpressed receptors (e.g., HER2, integrins, or folate receptors) on pathological cells. For example, agents targeting vascular endothelial growth factor (VEGF) or matrix metalloproteinases (MMPs) have shown promise for imaging tumor angiogenesis and metastasis (79,80). This molecular-level imaging may enable early detection, risk stratification, and monitoring of treatment response, moving MRI closer to personalized medicine. A major obstacle in these applications is represented by the low sensitivity of MRI contrast agents. Often the number of targeted epitopes is too low to yield sufficient change in the detected contrast-to-noise ratio in the acquired MR images. In the case of Gd-base agents, the local concentration has to be in the microM range, i.e. the number of Gd per cell has to be of the order of 10^9/relaxivity. However, these tasks continue to be challenged either pursuing systems endowed with marked relaxation enhancements and by applying supra-molecular approaches able to bring a large number of contrast agent units at the targeting sites.
- **Multifunctional (Theranostic) Agents**: Another cutting-edge approach involves theranostic nanoparticles—agents that combine diagnostic imaging and therapeutic delivery in a single platform. These hybrid systems often integrate contrast-generating components (e.g., gadolinium, manganese, or iron oxide) with chemotherapeutics, gene therapy vectors, or photothermal agents. Upon accumulation at the target site, such as a tumor, these agents enable real-time imaging and simultaneous localized therapy (81). For example, iron oxide nanoparticles functionalized with doxorubicin and tumor-targeting ligands have demonstrated dual capabilities for imaging and cancer treatment in preclinical models (82).
- **Reducing Gadolinium Toxicity**: To address the growing concerns regarding gadolinium retention in tissues, researchers have developed more stable gadolinium chelates—especially macrocyclic ligands—that tightly bind gadolinium ions and exhibit minimal *in vivo* dissociation (19). Furthermore, entirely gadolinium-free agents are being actively explored. Alternatives include manganese-based agents (which mimic calcium in biological systems and have natural clearance pathways) and iron oxide nanoparticles, which are biodegradable and pose a lower risk of long-term deposition (83). These developments represent important steps toward safer and more sustainable MRI contrast technologies. In this context, among the classes of non-metal containing agents, it is worth to mention diaCEST systems and hyperpolarized molecules as they are often based on naturally occurring species or compounds endowed with a high biocompatibility. Much attention is currently devoted to heteronuclear detection of hyperpolarized C-13 labelled molecules whose *in vivo* chemistry reports on ongoing enzymatic transformations at cellular level. This opens the way to investigate in real time important steps of cell metabolism as it has been shown in applications based on the use of hyperpolarized substrates like C-13-labelled pyruvate and fumarate.

Overall, these advances reflect a broader trend toward precision imaging, wherein MRI contrast agents not only enhance anatomical detail but also provide functional and molecular information critical for diagnosing and treating complex diseases.

8. CONCLUSION

Contrast agents are indispensable tools in the field of MRI, enhancing the diagnostic power of the imaging technique. They cause a marked signal enhancement in the regions where they distribute providing clearer, more detailed images of internal structures. Nowadays these CAs are used in about 30-40% of the MR scans acquired at clinical settings.

While there are risks associated with their use, ongoing advancements in contrast agent technology continue to improve both the safety and effectiveness of these agents. As research progresses, we are likely to see even more sophisticated agents that are safer, more targeted, and more efficient, further cementing MRI's role as a cornerstone of modern medical diagnostics.

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Research Article

Carl Schorlemmer (1834-1892) – The Red Chemist

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Abstract. This article presents the life and work of Carl Schorlemmer, one of the least remembered chemists in Organic Chemistry from the second half of the 19th century. His decisive investigation of alkanes as a basis for an organization of Organic Chemistry, other experimental investigations, his theoretical points of view, his activity as a historian of Chemistry and his relations with socialism are discussed.

Keywords: History of Chemistry, Organic Chemistry, Carl Schorlemmer, Alkanes, Historiography of Chemistry, Chemistry and Socialism.

INTRODUCTION

On July 1, 1892, chemist Carl Schorlemmer, professor of Organic Chemistry at the University of Manchester, who died on June 27, 1892, at his home in Manchester, aged 57, was buried in the Southern Cemetery in Manchester. The *Manchester Guardian* newspaper reported his death on June 28th; there is the obituary published in *Nature* by his friend Roscoe[1], the biographical article (1893) by Professor Harold Dixon (1852-1930)[2], the detailed biographical text by A. Spiegel in *Berichte*[3], but the obituary that is recorded in History is the article published by Friedrich Engels (1820-1895) in the July 3, 1892 edition of the newspaper *Vorwärts*, the official organ of the German Social Democratic Party: “Organic Chemistry was finally in a position to become a true science, based on an isolated pile of data, more or less incomplete, on the composition of organic compounds. Schorlemmer chose the simplest of these bodies as the object of his research, convinced that they lay the foundations of the new science: bodies initially formed by carbon and hydrogen, but by replacing part of the hydrogen with other simple groups or compounds, they transform into the most various substances. These are paraffins, the most important of which are found in petroleum, and from which alcohols, fatty acids, ethers, etc. can be obtained. What we know about these paraffins today we owe mainly to Schorlemmer. He analyzed the already known compounds of the paraffin series, separated them from each other, and obtained many of them for the first time in a pure state; the bodies possible according to the theory, but still unknown, he synthesized them too. He thus became one of the founders of current scientific Organic Chemistry"[4]. We should not be surprised by Engels' facility with scientific terminology, it results from long and detailed studies on science and especially the History of Science.

Engels' text, from which we extract only a part, is doubly important, both from a scientific and political point of view, with regard to the interaction between socialism and natural science. This possible relationship allows us to analyze some aspects of the practice of scientific research.

Schorlemmer is not much remembered in the history of 19th century Organic Chemistry, but that does not mean he is any less important. Apparently, the occupation with hydrocarbons, even more so with alkanes, seems to be a restricted topic, but Schorlemmer's exhaustive research work shows that this is not the case, that the topic is quite comprehensive.

ORIGIN AND TRAINING

Fig. 1 - Carl Schorlemmer (1834–1892), photographed by an unknown author. Courtesy of the Oesper Collection for the History of Chemistry, University of Cincinnati.

The oldest son of carpenter Johannes Schorlemmer, Carl Schorlemmer was born on September 30, 1834 in Darmstadt – the city that gave us other notable chemists, such as Liebig and Kekulé, and gave its name to element 110. After elementary school at the *Volksschule*, he attended the *Realschule*, and from 1850 to 1853, under his mother's influence and against his father's wishes, the School of Crafts (*Höhere Gewerbeschule*) in Darmstadt, where he learned the foundations of science. The father was against new studies, he wanted his son to occupy himself with practical activities.

At the suggestion of his friend Wilhelm Dittmar (1833-1892), in 1854 he went to work as a pharmacist's apprentice with the pharmacist Lindenborn in Gross-Umstadt, near Darmstadt. After two and a half years of activity, he passed the exam to practice as a pharmacist, which allowed him to take over a pharmacy in Heidelberg, *Schwan-Apotheke* (Swan Pharmacy). As a pharmacist, he attended classes taught by Robert Bunsen (1811-1899) at the University of Heidelberg, and his interest in Chemistry led him to leave pharmacy and enrol at the University of Giessen in 1859, where he studied with Heinrich Will (1812-1890) and also with Hermann Kopp (1817-1892), who transmitted to him his enthusiasm for the history of Chemistry. He only attended university for one semester: in 1859 he moved to England. He was 25 years old at the time, and from a young age he openly defended socialist ideas, which closed his path to academic life in his country, leading him to emigrate.

ARRIVAL IN ENGLAND

Fig. 2 - Carl Schorlemmer (1834–1892), photographed by Carl Spielmayer. From "The Rise and Development of Organic Chemistry" (1894). Courtesy of the Wellcome Foundation, London.

Fig. 3 - Sir Henry Enfield Roscoe (1833–1915), photographed circa 1880 by Walery (Stanislaw Ostorog, 1863–1929). Courtesy of the Wellcome Foundation, London (image in the public domain).

Like many German chemists who carried out their professional career partially (A.W.Hofmann, H.Caro, C.A.Martius) or entirely (P.Griess, L.Mond, H.Müller) in England, because of the advanced chemical industry that already existed there, also Schorlemmer went there, although for other reasons. Schorlemmer's entire scientific career was spent in England, and almost all of it in Manchester. As soon as he arrived, he was an assistant to the Scottish chemist Robert Angus Smith (1817-1894), an independent analyst in Manchester and one of the pioneers of Environmental Chemistry (creator of the concept of 'acid rain', 1852; chief inspector of the Alkali Inspectorate, 1863). Smith had studied with Liebig in Giessen from 1839 to 1841[5]. In 1861 luck smiled at Schorlemmer: he had become the assistant of Professor Henry Enfield Roscoe (1833-1915) at Owens College, the future University of Manchester, whose occupant, Wilhelm (William) Dittmar, almost a fellow countryman of Schorlemmer (he was from Gross-Umstadt), who had accepted an invitation from the University of Edinburgh. Before leaving for Scotland, he recommended the name of his friend Schorlemmer to Roscoe. From 1861 to 1873 Schorlemmer was Roscoe's 'demonstrator' and assistant, and in 1874 he became the first professor of Organic Chemistry at Owens College, a position he held until his death, thus taking over all teaching of Organic Chemistry, with Roscoe having the responsibility for Inorganic Chemistry (Owens College was founded in 1824, and after merger with other institutions it gave rise to Victoria University in Manchester in 1903). From assistant and collaborator, he became a close friend of Roscoe. Owner of an exceptional memory and vast knowledge, he was an excellent teacher, and his classes were highly appreciated by his students (he was then the only teacher of Organic Chemistry in England).

He remained single and died of lung cancer. A convinced socialist since his youth, he was a member of the Social Democratic Party of Germany (1889), and a close friend and scientific advisor to Friedrich Engels (1820-1895), who worked in Manchester in the family business (1844, 1856-1870), and Karl Marx (1818-1883). He spent holidays with Marx and Engels in London, traveled abroad with Engels and was one of thirteen people who attended Marx's funeral in London.

Fig. 4 - Statue in honor of Carl Schorlemmer, created by Heinz Beberniss (1920–2012) and erected in 1982 in front of the main entrance of the Leuna Industrial Complex in Merseburg. Courtesy of and photographed by www.merseburg-im-bild, reproduced with permission.

In 1879 he became a naturalized British citizen. He was a member of the Manchester Literary and Philosophical Society (1870), of the German academy *Leopoldina* (1887), since 1871 of the Royal Society (at the age of 34 a notable achievement), and of the American Philosophical Society (1878). He received an honorary doctorate from the University of Glasgow. In 1895, the Schorlemmer Memorial Laboratory, designed by the famous Victorian architect Alfred Waterhouse (1830-1905)[6], opened at Owens College. In Germany, the Merseburg Polytechnic (1954/1994) was named after "Carl Schorlemmer" (1964), and there is a bronze statue of Schorlemmer in Merseburg, by Heinz Beberniss (1920-2012), erected in 1972. In the decades from 1950 to 1970, in the former German Democratic Republic, Schorlemmer's life and work once again aroused the interest of historians, sometimes with hagiographic and out-of-context conclusions, because of his involvement with socialism.

SCHORLEMMER'S SCIENTIFIC WORK

Schorlemmer's experimental work in Organic Chemistry is not very vast, but exhaustive in the subjects it explores, also clarifying a series of theoretical aspects. His researches were published in more than 120 articles, which can be distributed into three groups:

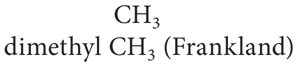
- investigations of hydrocarbons, mainly alkanes;
- investigation of other compounds in some way linked to hydrocarbons: alcohols, aldehydes, carboxylic acids and others;
- dyes and other loose items.

Investigations into hydrocarbons of the C_nH_{2n+2} series (alkanes)

Speaking of Schorlemmer brings to mind alkanes, and occupation with alkanes brings to mind Schorlemmer, the great authority on alkanes. From 1861 to 1871 Schorlemmer systematically studied alkanes (the name "alkane" was a proposal by August Wilhelm Hofmann, 1866), both from an experimental and theoretical point of view, and from the set of observations and conclusions regarding a group of compounds apparently little reactive, an impressive corpus of knowledge emerged about a group of organic compounds, to which as research progressed, Schorlemmer included what was already known about these compounds before him. The first alkane to be discovered was "swamp gas", our methane, collected in 1776 by Alessandro Volta (1745-1827) from the marshy waters on the shores of Lake Maggiore, where it is formed by anaerobic decomposition of submerged vegetables. John Dalton (1766-1844) also collected "swamp gas" (marsh gas, fire gas) from swampy waters, as shown in the mural by Ford Madox Brown (1821-1891) in Manchester City Hall.

In 1809, the chemist and mineralogist Johann Nepomuk von Fuchs (1774-1856) discovered in the oil of Tegernsee, in Bavaria, a solid residue that he called *Bergöl* or *Bergfett* (literally "mountain oil"), analyzed in 1820 by the pharmacist Johann Andreas Buchner (1783-1852). Better known became paraffin, discovered in 1830 by Karl von Reichenbach (1778-1869) in wood tar, and studied in 1832 in Giessen by Jules Gay-Lussac (1810-1877), son of Louis-Joseph Gay-Lussac and a student of Liebig, who determined a formula C_nH_{2n+2}, compatible with alkanes, but which Gay-Lussac interpreted as a mixture of C_nH_{2n} and hydrogen. The name 'paraffin' is from Reichenbach, meaning 'little reactivity' (*parum affinis*). The structure was determined in 1849 by Benjamin Brodie (1817-1880). The mineralogist Wolfgang Franz von Kobell (1803-1882), from the University of Munich, considered *Bergfett* to be identical to paraffin.

The first synthetic alkane was obtained in 1848 by Hermann Kolbe (1818-1884), who by electrolysis of sodium acetate obtained a C_2H_6 compound that he called "methyl" (our ethane). In 1850, Edward Frankland (1825-1899), treating methyl iodide CH_3I with sodium also obtained a compound C_2H_6, calling it 'methyl methide', also our ethane. Thus Schorlemmer himself in "Rise and Development of Organic Chemistry"[7] reports that the second simplest alkane, ethane, was thought to exist in two forms:



$$\text{dimethyl} \begin{matrix} CH_3 \\ CH_3 \end{matrix} \text{(Frankland)}$$

$$\text{ethyl hydride} \begin{matrix} C_2H_5 \\ H \end{matrix} \text{(Kolbe)}$$

Schorlemmer himself obtained ethane using the Frankland method, reacting diethylmercury with sulfuric acid, confirming the equality between the two forms[8].

Thus, this was the knowledge about alkanes when Carl Schorlemmer began his systematic investigations into hydrocarbons with the formula CnH_2n+_2 in 1861. He began his studies with the lighter fractions obtained from the distillation of coal tar, initially finding that the lighter fractions were identical to the light fractions from petroleum distillation[9]. The valid theory at the time, the type theory, reinforced by Edward Frankland's misinterpretations when studying hydrocarbons, predicted the existence of two series of compounds with the general formula C_nH_{2n+2}, alkyl hydrides and radicals.

In the case of C_7H_{16}, often cited by Schorlemmer, there were many possibilities of a hypothetical isomerism, for example:

C_7H_{15}	C_2H_5
H	C_5H_{11}
heptyl hydride	ethylpentyl

To analyze the behaviour of light tar compounds, he isolated pentane, hexane, heptane and octane, observing that when they react with chlorine, they all form monochlorides. He also suggested that Reichenbach's paraffin is a superior member of this series of compounds.

The chemical literature cites the study of the chlorination of methane by Marcellin Berthelot (1827-1907), giving rise to methyl chloride, which in turn allows many other derivatives to be obtained, and the method can be applied to methane homologues, thus being a general method of obtaining organic compounds[10]. Before Berthelot, the same method had been used by Schorlemmer to obtain heptyl acetate and heptyl alcohol, from the corresponding hydride[11].

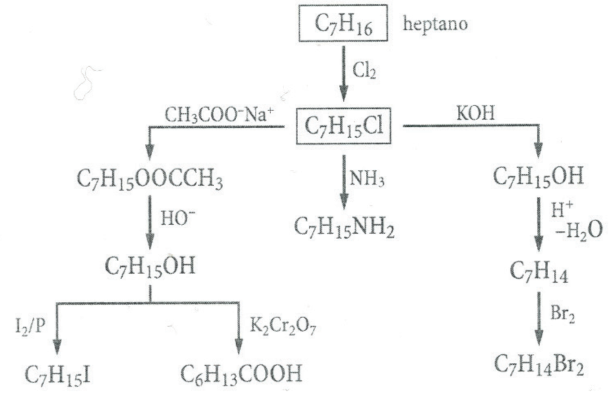


Fig. 5 - Organic compounds derived from heptane.

In the context of these investigations, Schorlemmer published in 1863 one of the most interesting articles in the history of Organic Chemistry, showing the incredible synthetic possibilities of heptane, normally considered to be very unreactive[12]. The Table shows the compounds obtained from 'heptyl hydride', with chlorination as the first step, according to a method developed by Hugo Müller (1833-1915), a German chemist active in London[13]. In a more theoretical field of this investigation, Schorlemmer managed to prove in 1864, with the aid of chlorination reactions, that there are no two series of C_nH_{2n+2} compounds in the hydrogen type. Analyzing the halogenation products, for example, 'heptyl hydride' and 'ethylpentyl', the formation of the same chloropentane is always observed. Chlorination of 'ethylpentyl' does not form ethyl chloride and pentyl chloride. There is, therefore, only one series of hydrocarbons with the general formula C_nH_{2n+2}, that is, 'hydrides' and 'radicals' are identical. This discovery was fundamental for a correct systematization of alkanes[14].

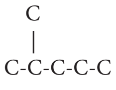
Just as he studied heptane and heptane derivatives from different sources (petroleum and coal tar), Schorlemmer also studied amyl compounds derived from pentane obtained from petroleum, and compared them with the same compounds obtained from fusel oil that accompanies amyl alcohol, obtained by Scheele in 1775 by fermentation (today it is known that it is isoamyl alcohol). He found that in both cases the physical constants of derivatives such as amyl chloride (B.P. 101°C), amyl alcohol (B.P. 132°C), ethyl ester (M.P. 140°C) were identical. These studies seem at first glance to be of no greater importance, but this step-by-step process involving qualities and composition/structure of derivatives of simpler compounds in Organic Chemistry were essential in helping to establish the foundations of this discipline. Schorlemmer arranged the data in a table[15]:

AMYLIC COMPOUNDS				
	FROM FUSEL OIL		FROM PETROLEUM PENTANE	
	M.P.	density	M.P.	density
C_5H_{12}			34°C	0,6263 at 17°C
$C_5H_{11}Cl$	101°C	0,8750 at 20°C	101°C	0,8777 at 20°C
$C_5H_{11}O$				
C_2H_3	140°C	0,8733 at 15°C	140°C	0.8752 at 15°C
$C_5H_{12}O$	132°C	0,8148 at 14°C	132°C	0,8199 at 14°C

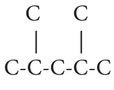
Based on this possibility of systematization, in 1868 Schorlemmer proposed a classification of these compounds into groups: alkanes[16] with one, two or three carbons do not present isomers; those with more than four carbons are classified into groups: in the first group, the carbon atoms form normal chains; in the second group, one carbon atom is linked to three others (isopropyl group); in the third group, there are two isopropyl groups; in the fourth group, one carbon atom bonds to four others.

$C-C-C-C-C$

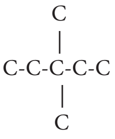
1st group


$C-\overset{\overset{C}{|}}{C}-C-C-C$

2nd group


$C-\overset{\overset{C}{|}}{C}-C-\overset{\overset{C}{|}}{C}-C$

3rd group


$C-C-\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}-C-C$

4th group

Thanks to this theoretical innovation by Schorlemmer, it was possible to understand the isomers of alkanes, and include alkanes synthesized by other chemists, such as Wurtz, Erlenmeyer, Butlerov, Friedel, Ladenburg, in the list of these compounds. Schorlemmer has already noticed the difference in reactivity at carbons 1 and 2 of the chain: in octane, for example, the substitution ratio at carbons 1 and 2 is 1:5 (current data: 1:4.3). It was also possible to establish a relationship between boiling points and structure, along the lines predicted by Hermann Kopp (1817-1892) in 1845[17]. This relationship is also useful for the classification of new alkanes. The amount of information obtained allows us to evaluate the great importance of Schorlemmer's article for the evolution of Organic Chemistry. The growing acceptance of Kekulé's structural theory drove alkane research forward, and Carl Magnus von Hell (1849-1926) in 1889 synthesized the hitherto longest alkane, hexacontane $C_{60}H_{122}$. Friedrich Krafft (1857-1923) had synthesized in 1888 a series of higher normal-chain paraffins[18]. A theoretical explanation for all these phenomena was not possible in the context of classical Organic Chemistry, but they could all be explained by the Ingold-Hughes electronic-structural theory, as first and second order nucleophilic substitutions (SN_1 or SN_2) and involving free radicals or carbocations as intermediates.

Oil

Schorlemmer's research on alkanes began with the light fractions obtained in the destructive distillation of coal, mainly the C4 – C8 fraction. Then, for comparison, he researched petroleum distillation derivatives[19]. Samples of North American oil had already been studied by Théophile Jules Pelouze (1807-1878) and Auguste Cahours (1813-1891), who in 1861/1862 isolated pentane, hexane and heptane[20]. Lacking larger quantities of Pennsylvania oil, Schorlemmer used samples of Canadian oil. After distillation and several purification procedures, four compounds were obtained[21] from the fraction distilling below 129° C:

Amyl hydride	$C_{10}H_{12}$	B.P. 39° C	(pentane)
Hexyl hydride	$C_{12}H_{14}$	B.P. 68° C	(hexane)
Heptyl hydride	$C_{14}H_{16}$	B.P. 98° C	(heptano)
Octyl hydride	$C_{16}H_{18}$	B.P. 119° C	(octane)

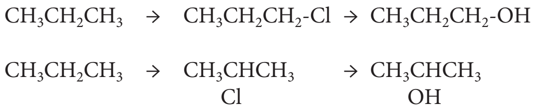
The chemical behavior of normal-chain paraffins was subsequently studied and published in several articles in *Philosophical Transactions*:[22] Part I, in 1872; Part II, in 1878; Part III, in 1880; Part IV (with T. E. Thorpe, on *Pinus* heptane), in 1883. In summary, the conversion of paraffin successively into chloride, then into primary or secondary alcohol, then into carboxylic acid or ketone, by known methods is discussed.

Coincidentally, at the same time that Schorlemmer began to study saturated hydrocarbons, the petroleum industry began, in 1846 in the Caucasus and Canada, in 1854 in Galicia (Austria), in 1858 in Germany and the United States. Exploration and the oil industry had scientific guidance from chemists such as Dimitri Mendeleev (1834-1897), Vladimir Markovnikov (1838-1904), Alexander Butlerov (1828-1886), Carl Engler (1842-1925). There was no direct participation by Schorlemmer in the oil industry.

Schorlemmer's other research activities

Although Schorlemmer is considered the "chemist of alkanes", much more of his research must be recorded, often in some way linked to alkanes. It is not intended to present an exhaustive list of Schorlemmer's experiments, but some interesting cases deserve a more detailed comment.

In 1868, he independently demonstrated that there are two alcohols derived from propane, propyl alcohol and isopropyl alcohol, obtained simultaneously but in different proportions. Initially, propane is treated with chlorine, obtaining 1-chloropropane and 2-chloropropane (the latter predominates). The reaction of these with caustic soda forms propyl alcohol (new preparation method) and isopropyl alcohol respectively:



$$CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2\text{-}Cl \rightarrow CH_3CH_2CH_2\text{-}OH$$

$$CH_3CH_2CH_3 \rightarrow \underset{Cl}{CH_3CHCH_3} \rightarrow \underset{OH}{CH_3CHCH_3}$$

He also found that the main product is, however, propylene dichloride, and that in the case of later alkanes there is always a substitution by chlorine on carbons 1 and 2. In the reaction of alkanes, substitution only occurs on carbon 2 (it is known today that minimal substitution also occurs on carbon 1). Alcohols could be identified through their oxidation products[23]. As before, the electronic-structural theory of Organic Chemistry explains these facts, which for Schorlemmer were empirical data, although proven. Schorlemmer also carried out chlorination at higher temperatures, between 100 and 200 °C, when trichlorohydrin $C_3H_3Cl_3$ and tetrachloropropane were formed, among other products that were not identifiable at the time[24]. In "sextane" (= hexane) and other alkanes it was not possible to replace more than six hydrogen atoms with chlorine (a fact also observed by Pelouze and Cahours).

He also developed a procedure for converting isopropyl derivatives into normal propyl derivatives[25].

Alcohol obtained from castor oil

One of the natural products most studied by chemists is castor oil (*Ricinus communis L.*), perhaps because it has been used for thousands of years, but I believe that the motivation was the uncertainty about which products were formed during its decomposition. Schorlemmer also played a part in solving the problem. Schorlemmer wrote: "There is perhaps no other known compound that is more frequently and exhaustively studied by various chemists, and yet whose structure is clouded by obscurity, than the alcohol obtained by distilling castor oil in the presence of caustic soda.[26]" The most accepted by chemists of that time were caprylic alcohol (octanol) and enanthic alcohol (heptanol).

For his doctoral thesis (1856), French pharmacist Jules Bouis (1822-1886)[27] studied castor oil in detail, including oxidation with a weak solution of nitric acid, in which sebacic acid and an alcohol are formed, which he identified as caprylic alcohol (octanol). He prepared derivatives of caprylic alcohol and studied its properties (1855)[28]. In another decomposition of castor oil, Bouis obtained not caprylic alcohol, but enanthic alcohol (heptanol)[29]. The Englishman Ernest Chapman also reports in 1865, as recorded by Schorlemmer, the formation of caprylic alcohol and enanthic alcohol in the decomposition of castor oil[30]. And where is Schorlemmer's participation? Hermann Kolbe (1818-1884), from the fragments obtained in the oxidation of the oil, suggests that a secondary alcohol must be formed, probably methylhexylcarbinol, which upon oxidation leads to a ketone. Schorlemmer considers Kolbe's interpretation correct, stating his conclusions in an article (1868)[31].

In Bouis's opinion, the first to chemically investigate castor oil was Alexandre Bussy (1794-1882), with his collaborator Louis René Le Canu (1800-1871)[32], in 1848. By distillation under reduced pressure, they obtained from the decomposition of the acid ricinoleic (the main constituent of castor oil, about 90%) heptanal and undecylenic acid, a reaction of commercial interest.

Friedrich Krafft (1852-1923), reviewing this entire subject, published an article on the distillation of castor oil under reduced pressure[33].

Ricinoleic acid $CH_3\text{-}(CH_2)_6\text{-}CH_2OH + HOOC\text{-}(CH_2)_8\text{-}COOH$	Bouis, 1855
Ricinoleic acid $CH_3CH(OH)\text{-}C_6H_{13} + HOOC\text{-}(CH_2)_8\text{-}COOH$	Kolbe, 1868 Schorlemmer
Ricinoleic acid $CH_3\text{-}(CH_2)_5\text{-}CHO + CH_2{=}CH\text{-}(CH_2)_8\text{-}COOH$ [in our notation]	Bussy, 1848

Formation of cetyl alcohol

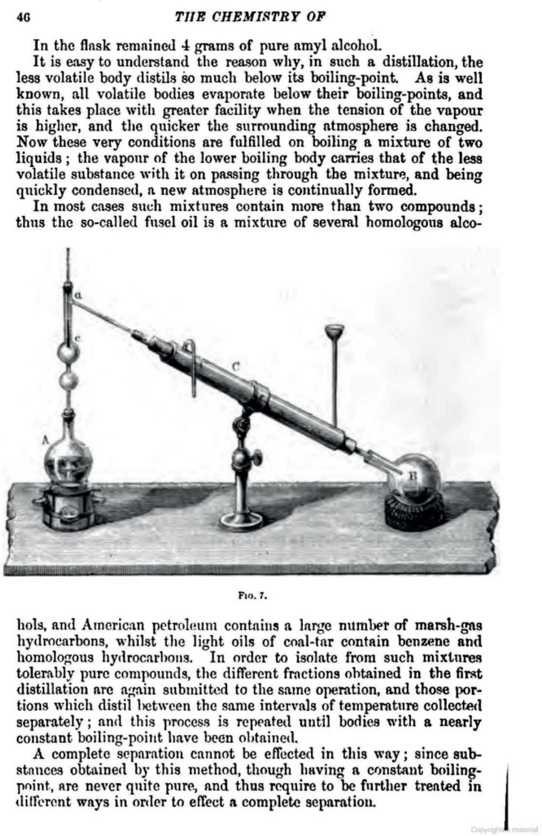
Let us finish this part of the description of Schorlemmer's work with an unusual procedure for the formation of cetyl alcohol. Warming sebacic acid, $C_{10}H_{18}O_4$, with barium hydroxide, $Ba(OH)_2$, the hydrocarbon C_8H_{18} and several other compounds are formed. A white crystalline compound, after purification, showed the properties of alcohols, and after analysis, it was found to be cetyl alcohol, $C_{16}H_{33}OH$. The obtaining of octane from sebacic acid finds other records in Organic Chemistry, including by Schorlemmer himself, but the formation of cetyl alcohol in this reaction is indeed surprising[34] (cetyl alcohol was discovered in 1817 by Chevreul).

Other research

In addition to the themes mentioned, Schorlemmer and collaborators dealt with others, although less intensively. With his student R. S. Dale he studied the aurine dye, and its transformation into rosaniline[35], with eight publications between 1871 and 1879; there are studies on suberone[36] (1874), on suberic and azelaic acids[37] (1879). There are also isolated investigations into a new method of obtaining methane (1873), into the boiling points of some paraffins and their derivatives (1872), among others.

SCHORLEMMER AUTHOR

From the beginning of the 1880s Schorlemmer began to dedicate himself more and more to his texts, leaving aside his laboratory activity. In addition to smaller writings, he left two major works of permanent importance in the historiography of Chemistry, one of them in partnership with his colleague and friend Henry Enfield Roscoe (1833-1915). Roscoe and Schorlemmer published from 1877 onwards an exhaustive treatise on Chemistry, simultaneously in German and English, "*Ausführliches Lehrbuch der Chemie*" in German, "*A Treatise on Chemistry*" in English. The first volume was initially published in German, in 1877, by *Friedrich Vieweg & Sohn*, Braunschweig, and in 1878 in English, by *D. Appleton and Company*, New York. Volume II followed in 1879, volume III in 1884, volume IV in 1886. Volume V was published in 1896, after the death of Schorlemmer, who was replaced by Julius Wilhelm Brühl (1850-1911), professor at Heidelberg. In volumes VI (1898), VII (1900), VIII (1901) and IX (1901), Julius Brühl replaced Schorlemmer in what is now "*Roscoe-Schorlemmers Ausführliches Lehrbuch der Chemie*". Mention should also be made of the collaboration, from volume V onwards, of the Finns Edvard Hjelt (1855-1921) and Ossian Aschan (1860-1939). Volume I has a 34-page preface on the history of chemical science, and in the other topics there is always information of a historical nature.



46 *THE CHEMISTRY OF*

In the flask remained 4 grams of pure amyl alcohol.

It is easy to understand the reason why, in such a distillation, the less volatile body distils so much below its boiling-point. As is well known, all volatile bodies evaporate below their boiling-points, and this takes place with greater facility when the tension of the vapour is higher, and the quicker the surrounding atmosphere is changed. Now these very conditions are fulfilled on boiling a mixture of two liquids; the vapour of the lower boiling body carries that of the less volatile substance with it on passing through the mixture, and being quickly condensed, a new atmosphere is continually formed.

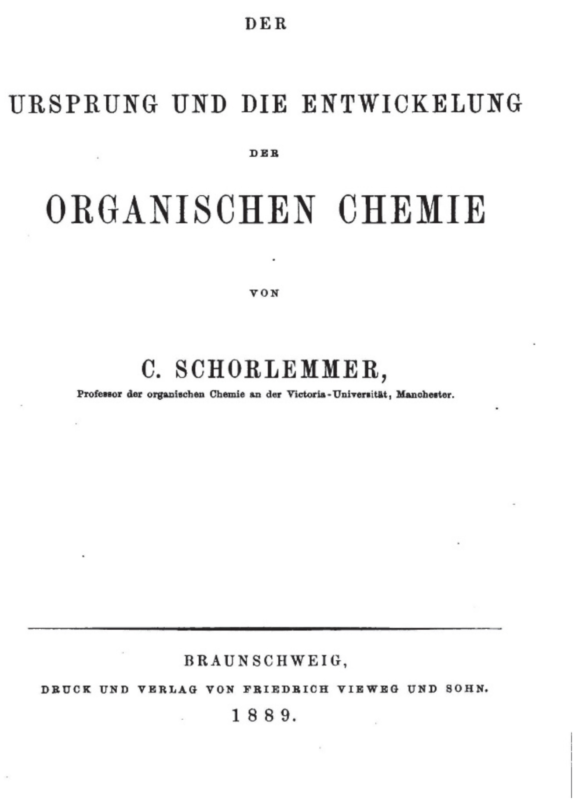
In most cases such mixtures contain more than two compounds; thus the so-called fusel oil is a mixture of several homologous alcohols, and American petroleum contains a large number of marsh-gas hydrocarbons, whilst the light oils of coal-tar contain benzene and homologous hydrocarbons. In order to isolate from such mixtures tolerably pure compounds, the different fractions obtained in the first distillation are again submitted to the same operation, and those portions which distil between the same intervals of temperature collected separately; and this process is repeated until bodies with a nearly constant boiling-point have been obtained.

FIG. 7.

A complete separation cannot be effected in this way; since substances obtained by this method, though having a constant boiling-point, are never quite pure, and thus require to be further treated in different ways in order to effect a complete separation.

Fig. 6 - Page 46 of Carl Schorlemmer's book, "The Chemistry of Organic Compounds", depicting equipment for fractional distillation.

The second work of importance is a work linked to the History of Chemistry, more precisely to the history of the chemistry of carbon compounds, "*The Rise and Development of Organic Chemistry*", published in Manchester in 1879. In 1885 a French translation appeared, "*Origine et Dévelopement de la Chimie Organique*", published in Paris, translated by Alexandre Claparède (1858-1913); a German edition dates from 1889 ("*Der Ursprung und die Entwicklung der Organischen Chemie*", in the *Ostwalds Klassiker* series no. 259), which served as the basis for the second English edition (1894), edited by Arthur Smithells (1860-1939), a student of Schorlemmer.



DER

URSPRUNG UND DIE ENTWICKELUNG

DER

ORGANISCHEN CHEMIE

VON

C. SCHORLEMMER,

Professor der organischen Chemie an der Victoria-Universität, Manchester.

BRAUNSCHWEIG,

DRUCK UND VERLAG VON FRIEDRICH VIEWEG UND SOHN.

1889.

Fig. 7 - Front page of "Der Ursprung und die Entwickelung der Organischen Chemie", published by Friedrich Vieweg in Braunschweig, 1889.

Another work by Schorlemmer that was important in its time was a textbook on Organic Chemistry, "*Lehrbuch der Kohlenstoffverbindungen oder der Organischen Chemie*" (which is also part of the "*Ausführliches Lehrbuch*"), published in Braunschweig in 1871. It is a very detailed text, written in a simple style, easy and pleasant to read.

Schorlemmer's first publications were translations into German of works by Henry Roscoe: in 1867, "*Elementary Lectures in Chemistry*", a kind of abstract for the later "*Treatise on Chemistry*". And in 1870 "*Spectrum Analysis*", published in English in 1869 (*Macmillan*, London).

SCHORLEMMER AS HISTORIAN OF CHEMISTRY

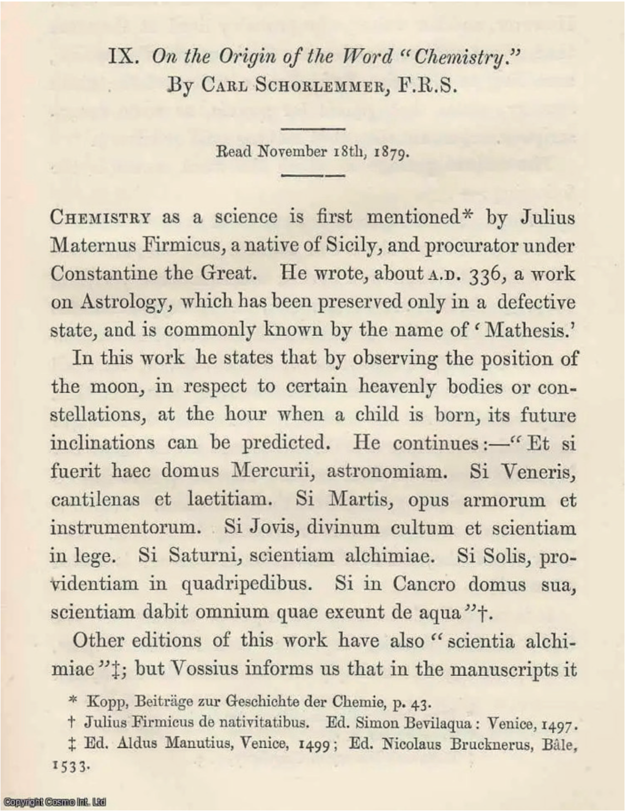
During the short period of studies in Giessen, Schorlemmer was a student of Hermann Kopp (1817-1892), perhaps the most important historian of Chemistry in the 19th century ("*Geschichte der Chemie*", 4 volumes, 1843/1847, with three supplements, and other texts), who was his inspiration in this field: he dedicated his "*Rise and Development of Organic Chemistry*" to Kopp.

Organic Chemistry had recently abandoned the dualism of the *Naturphilosophie* of Friedrich von Schelling (1775-1854) and his followers (in the sciences, names such as Hans Christian Oersted [1777-1851], Johann Wilhelm Ritter [1776-1810], Karl Wilhelm Kastner [1783-1857]), the theory of radicals was gradually converted into the theory of types (incorporating radicals into different types), when Schorlemmer decided to deal with the history of this branch of Chemistry, in 1879. Schorlemmer's experimental work in turn removed types from the scene, paving the way for carbon chain structures, in accordance with the proposals of Kekulé or Couper. The extensive text (more than 600 pages) "*Lehrbuch der Kohlenstoffverbindungen oder der Organischen Chemie*" (1871) does not present any historical data. The first 33 pages of the "*Ausführliches Lehrbuch*" (1871) present a summary of the History of Chemistry from Greek Antiquity up to the times of Liebig[38]. For historian Karl Heinig, Schorlemmer's biographer[39] (1974), the purely empirical data that followed the results explained by *Naturphilosophie* (the "plague of science", in Liebig's words), caused disenchantment in Schorlemmer, who found a viable alternative in adopting a point of view of dialectical materialism, and for Heinig this work by the "red chemist" would be the first chemical history in accordance with this ideology. The greatest concern was dedicated to "the basic laws of scientific development, the context in which isolated sciences interact with each other, theoretical questions about the role of hypotheses and theories, and the connection between theory and *praxis*"[40].

Chemical transformations must be seen as being dynamic, and in the wake of Heraclitus' thought, for whom the only real and eternal thing is transformation, that is, the dynamic visualization of chemical phenomena. At the same time that Schorlemmer's work appeared, many organic chemists wrote the history of their specialty, limiting themselves, however, to the simple report of empirical facts. Schorlemmer takes sides in these discussions, returning to value the philosophical aspects contained in experiments, banned from the practice of Chemistry because of the exaggerations of *Naturphilosophie*. He defends his points of view in the face of the discordant or even contrary point of view of the majority of organic chemists of the time, for example, condemning the exaggerated importance given to pure and simple empirical fact, an exaggeration that for Engels is "the surest way to arrive at from natural sciences to mysticism"[41]. He sought to overcome pure empiricism and remaining mechanism, a task which was facilitated by his great erudition and ease in finding connections between facts.

For Schorlemmer, the history of Chemistry is not just a report of what happened, but a discussion of the processes that led to the development of theories and experimental procedures, a discussion based on the economic and philosophical conceptions in force at each time. Knowledge of the history of Chemistry is essential for understanding Chemistry itself, and at the time in question, Organic Chemistry investigated subjects that involve dynamic situations, tautomerism for example[42].

For Schorlemmer, without a theoretical basis it is not possible to achieve scientific progress, which was particularly important at a time when "new discoveries emerge in science every day". And as a historian, he sought to show that the development of science requires certain assumptions, such as, in his opinion, dialectical argumentation. Quoting Schorlemmer, "a new science does not appear suddenly, like Minerva from the head of Jupiter, nor does it appear in its full beauty, like Venus born from the foam of the waves".[43] Schorlemmer defends the position that "a scientific theory is not a dogma, but changes over time, in accordance with the laws of dialectics"[44].



IX. *On the Origin of the Word "Chemistry."*
By Carl Schorlemmer, F.R.S.

Read November 18th, 1879.

Chemistry as a science is first mentioned* by Julius Maternus Firmicus, a native of Sicily, and procurator under Constantine the Great. He wrote, about A.D. 336, a work on Astrology, which has been preserved only in a defective state, and is commonly known by the name of 'Mathesis.'

In this work he states that by observing the position of the moon, in respect to certain heavenly bodies or constellations, at the hour when a child is born, its future inclinations can be predicted. He continues:—"Et si fuerit haec domus Mercurii, astronomiam. Si Veneris, cantilenas et laetitiam. Si Martis, opus armorum et instrumentorum. Si Jovis, divinum cultum et scientiam in lege. Si Saturni, scientiam alchimiae. Si Solis, providentiam in quadripedibus. Si in Cancro domus sua, scientiam dabit omnium quae exeunt de aqua"†.

Other editions of this work have also "scientia alchimiae"‡; but Vossius informs us that in the manuscripts it

* Kopp, Beiträge zur Geschichte der Chemie, p. 43.
† Julius Firmicus de nativitatibus. Ed. Simon Bevilaqua: Venice, 1497.
‡ Ed. Aldus Manutius, Venice, 1499; Ed. Nicolaus Brucknerus, Bâle, 1533.

Fig. 8 - First page of Carl Schorlemmer's paper, "Origin of the Word Chemistry".

In addition to his masterwork, Schorlemmer published three articles on historical topics: "Origin of the Word Chemistry" (1882)[45], "The History of Creosote, Cedriret and Pittacal" (1889)[46], "On the History of Artificial Preparation of Indigo" (1881)[47]. The second of these articles is particularly rich in historical and chemical information, from the perspective of the time.

When he passed away, Schorlemmer left an incomplete 1100-page manuscript of a work on the History of Chemistry, entitled "*Beiträge zur Geschichte der Chemie*", the result of years of research. The manuscript covers the history of Chemistry from Antiquity to the mid-17th century, and in Rolf Gelius' opinion, in it Schorlemmer "surpasses the heights of historical-scientific efficiency". Some historians want to see in these "*Beiträge*" the intention of writing a universal history of Chemistry from a Marxist point of view, but Gelius does not share this interpretation. The administrator of Schorlemmer's legacy, Louis Siebold (1838-1901), tried to continue the work, but soon gave up. The manuscript, preserved in Manchester's *John Rylands University Library*, remains unpublished to this day[48].

SCHORLEMMER, SCIENCE AND SOCIALISM

Schorlemmer, "the first Marxist among chemists and the first chemist among Marxists", did not suddenly awaken to the interests of the working class, but, as we have already said, since his youth he defended socialist thought, to which he always remained faithful, which made an academic career in his homeland unfeasible. In 1889 he formally joined the Social Democratic Party of Germany. His friendship with Engels and Marx, for whom he was a scientific 'advisor', has also been mentioned.

Marxist-oriented historiography wants to see in Schorlemmer's research typical examples of "dialectic-materialist" research. In fact, there is nothing different about Schorlemmer's laboratory activity when compared to the activity of other researchers of the time, far from socialism, such as Dumas, Wurtz, Hofmann or Kekulé. Nor can it be said, as Karl Heinig would have it, that in his experimental data he "saw beyond" the 'greats' of his time, such as Liebig, Hofmann or Emil Fischer[49]. The only difference that could be pointed out, but which would not lead to a different working methodology, would be the status of the structure, considered by Schorlemmer, as well as by Butlerov, as being real, while Kekulé and Couper considered the structure to be a model or abstraction.

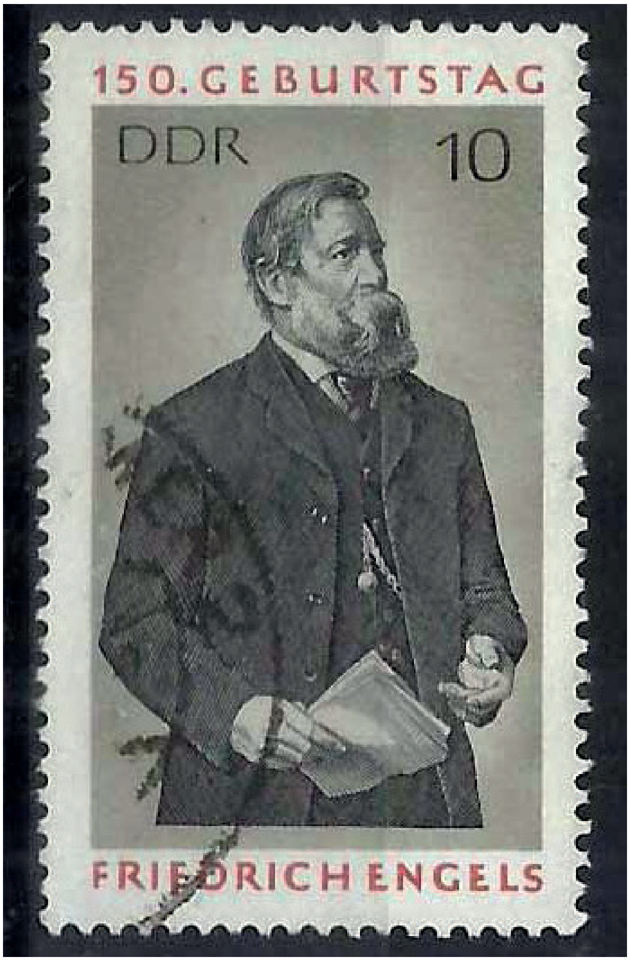


Fig. 9 - Stamp issued by the former German Democratic Republic in 1970, commemorating the 150th birthday of Friedrich Engels (1820–1895).

In fact, there is no "socialist science", as the criteria of scientificity are independent of ideologies. What ideological positions can influence is "doing science", from choosing the topic to applying the research results. Defenders of a "socialist science" refer to ideas already present in Hegel, the conversion of quantity into quality, present, for example, in the homologous series of alkanes. Karl Marx writes, when dealing with the concept of 'surplus value', that "here, as in the natural sciences, the validity of the rule discovered by Hegel in his 'Logic' that quantitative only transformations become, at a given point, qualitative transformations"[50]. Schorlemmer writes about this, citing Engels' "Anti-Dühring": "Each new member comes into existence by the addition of a unit – CH_2 – to the immediately preceding molecule" and that "this quantitative modification in the molecule each time produces a qualitatively different body". This idea is quite common in Organic Chemistry, it exists, for example, in the variation of melting points and boiling points of a homologous series as the molecular mass increases, a subject studied by Hermann Kopp (1817-1892) since 1841, and by other organic chemists. This Hegelian idea also exists outside of science, in literature for example, as in the beautiful passage by José Saramago (1922-2010), taken from "Memorial do Convento" (1982, English translation "Baltasar and Blimunda", 1988): "In total I heard that five hundred arrived. So many, Blimunda is amazed, and neither one nor the other knows exactly how many there are five hundred, not to mention that the number is the least exact of all the things in the world, it is said five hundred bricks, five hundred men, and the difference there is between brick and man is the difference that is thought not to exist between five hundred and five hundred... "[51].

SOME CONCLUSIONS ABOUT SCHORLEMMER'S EMPIRICAL WORK

At first glance Schorlemmer appears to be one of the many organic chemists active in the second half of the 19th century, chemists that Thomas Kuhn would define as practitioners of "normal science". However, a more in-depth analysis shows that this is not the case. Schorlemmer's empirical and experimental activity leads us to conclusions that go beyond the mere accumulation of information about organic compounds.

The apparently exclusive occupation with a restricted group of organic compounds (aliphatic hydrocarbons, mainly alkanes) seems to suggest the investigation of a few similar compounds, but the detailed study of the properties of these simplest compounds in Organic Chemistry, to which Schorlemmer subjected these compounds, extends to other compounds, with other chemical functions, as seen before with the study of heptane. It is evident that Organic Chemistry can be structured from these simplest compounds, alkanes.

Schorlemmer also shows that organic compounds such as alkanes can be obtained, with exactly the same properties, from different natural materials, such as petroleum and mineral coal. In this case of alkanes, an approximation between Organic Chemistry and Inorganic Chemistry is observed, going against Lavoisier's ideas that there is no fundamental difference between inorganic and organic compounds.

Going a little further, Schorlemmer showed that not only can different organic compounds be obtained from different species or genera, but that there are organic compounds that can be obtained from both the inorganic and organic worlds, and presents as an example (iso) amyl alcohol, obtained either from pentane in petroleum or coal, or through fermentation processes, which are clearly organic. We have a further proof that there is no "vital force", expanding the proofs of Friedrich Wöhler with the synthesis of urea (1828), and Hermann Kolbe, with the total synthesis of acetic acid (1845).

With these examples, we can say that Schorlemmer's experiments go beyond the limits of Organic Chemistry, inserting it into the theoretical field of 19th century Chemistry. As we have said before, historians faithful to Marxist ideas want to see an ideological component in Schorlemmer's experimentation, which would lead to a "socialist science", something that simply does not exist. The Hegelian concept of converting quantity into quality could be a starting point for a "socialist science". What we understand here by "socialist science" has nothing to do with the refusal to accept the theory of resonance or Mendelian genetics by official Soviet science authorities. The theory of resonance, initially accepted, was later rejected as being 'ideologically untenable', primarily by the president of the Academy, Alexander Nesmeyanov (1899-1980), which did not prevent all Soviet scientists from sharing this refusal. A conversion of quantity into quality is visible in the gradual variation of the boiling points of alkanes with increasing molecular weight, or the number of carbon atoms in a normal chain:

Number of carbons	Compound	B. P. (°C)
1	methane	-161
2	ethane	- 87
3	propane	- 42
4	butane	0,5
5	pentane	36
6	hexane	69
7	heptane	98
8	octane	125
9	nonano	151
10	decane	171

In fact, this gradual variation of physical constants (M.P., P.E., density) as a function of molecular mass (indirectly with the number of carbon atoms) had already been studied since 1841 at the University of Heidelberg by Hermann Kopp (1817-1892), a scientist who has nothing socialist about him. Kopp's studies were purely experimental, with attempts to establish mathematical expressions to calculate boiling points. Kopp's most comprehensive study on the relationship between physical constants and molecular weight, in several homologous series (alcohols, carboxylic acids, ethers) moves away from the idea of a simple conversion of quantity into quality, as the 'molecular weight' of the compounds is being considered, and not their structure, something still unknown at the time of Kopp's studies[52]. Also in Schorlemmer's time, the effects of structure on the variation of physical constants were still unknown: see, for example, the variation in the M.P. of alkanes with a normal chain, remembering that the chain is not linear.

CONCLUSION

The majority of chemists active in the second half of the 19th century were concerned with Organic Chemistry, the area of Chemistry that was then developing the most, perhaps stimulated by the gradual development of a theoretical basis for understanding the behavior of organic compounds, also due to the infinite variety of natural products awaiting study, and the growing interest in pharmaceuticals and dyes, or, simple scientific curiosity.

Some of these many organic chemists were distinguished by some particularity. In Schorlemmer's case, through the exhaustive investigation of the simplest organic compounds, the alkanes, the basis is laid for a classification of organic compounds, and later for their systematic nomenclature. The systematic study carried out by Schorlemmer ended up leading to theoretical aspects, as an example of the evolution of the theory from radicals to types and later to structures, inserting Organic Chemistry into the field of Chemistry as a whole.

The idea that a theory is necessary for the development of a science, combined with his dialectical-materialist worldview based on Hegel's philosophy, led him to what some historians have come to call "socialist science", in fact an experimentation based on theoretical concepts, not necessarily materialist or dialectical, which differed from a solely empirical experimentation, such as that of Hermann Kolbe (1818-1884), enemy of any theory in experimentation, defender of an empiricism that borders on dogma, which did not prevent him from leaving as a legacy an immense scientific production, of great importance in the development of Organic Chemistry.

This comparison shows the importance of different ways of approaching the universe of organic compounds. It shows the importance of researchers like Schorlemmer, and others who also distinguished themselves by a different approach or a particular aspect in their practice of "normal science".

Also, one cannot forget Schorlemmer's concern for social issues, witnessed by his membership in the German Social Democratic Party. It is not without reason that he felt himself at home at *Owens College*, which offered studies to those who found themselves excluded from Oxford and Cambridge, because they did not have possessions or did not belong to the social elite. With 62 students, *Owens College* opened its doors in 1851, founded with resources donated by Manchester merchant John Owens (1790-1846), who died unmarried. Owens friend, the manufacturer George Faulkner (c.1790-1862) refused to be his heir, to allow the foundation of a College independent from the religious ties which existed in Oxford and in Cambridge. Faulkner was the first chairman of the trustees of the *Owens College*. Since 1880 the *Owens College* is part of the *Victoria University* of Manchester[53].

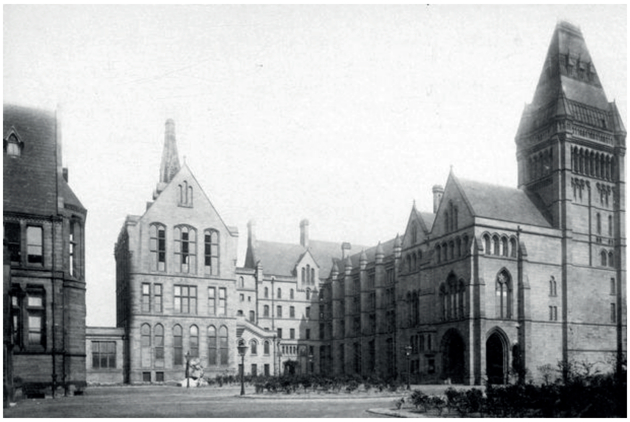


Fig. 10 - Owens College, Manchester, from "The Owens College, Manchester (founded 1851): A Brief History of the College and Description of the Various Departments", by Philip Joseph Hartog (1864–1947). Published by J. Cornish, Manchester, 1900 (page 58).

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Research Article

Pictorial-Based Learning (PcBL): Fostering Students' Argumentation Skills and Understanding of Chemistry

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Abstract. This study highlights the implementation of Pictorial-Based Learning (PcBL) in basic chemistry classes and assesses its contribution to students' argumentation skills and understanding of chemistry. Thirty-five students aged 19-21 years enrolled in general chemistry, covering solubility & intermolecular forces, gas laws, kinetic molecular theory, and thermochemistry, at Universitas Negeri Malang, East Java, Indonesia, participated in this study. The intervention was conducted over one term/semester. Students' argumentation skills were assessed at the end of each topic and classified using Toulmin's Argument Pattern (TAP), which comprises claims, data, warrants, backing, and rebuttals. This study uncovered the following outcomes. The implementation of PcBL contributed to improving students' argumentation skills. However, no students demonstrated the highest level (5). Most students' argumentation skills ranged from Level 3 to Level 4, with Level 3 being the most common. Therefore, it implies an adequate contribution of the approach in improving students' argumentation skills. However, the correlation between students' argumentation skills and their understanding of chemistry was not substantial. This study amplifies the need for the PcBL in broader chemistry teaching across cohorts and topics. Its contribution to forming other students' soft skills is also a worthwhile future exercise.

Keywords: Model and Modelling in Chemistry, Visualisation, Scientific Argument, Deep Understanding

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1. INTRODUCTION

School systems around the world are being urged to create frameworks that emphasise acquiring skills, knowledge, and attitudes required for success in the twenty-first century [1]. A more complex society and a quickly changing technology-based economy have presented new and challenging problems to schools and communities alike [1] required for personal, occupational, and social inclusion [2]. Therefore, chemistry instruction should be delivered from a perspective that fosters students' robust understanding of chemistry and develops their 21st-century skills, including scientific argumentation. Using scientific argumentation in education is crucial, as it enhances students' engagement in the teaching and learning process and enables them to develop their ideas by exploring their own thoughts rather than presenting them in pre-existing templates [3].

Building scientific arguments is critical for all scientists, regardless of their field [4]. Students' involvement in an argumentative environment can lead to a better understanding of a relevant concept [5]. Students' argumentation skills and critical thinking positively contributed to their understanding of fundamental biology concepts. [6]. Science for citizenship must stress how science works, and students should be given opportunities to study science-in-the-making, assess evidence, and examine arguments that entail uncertainty [7].

Students' argumentation skills have been a concern in education worldwide for the last decade.[8] Empirical data, rather than just theoretical discourse, highlight the beneficial impact of argumentation on student learning within science education [9]. Unfortunately, many teenagers and even adults do not exhibit promising argumentation skills [10]. The findings suggest that students require additional assistance in using evidence and reasoning effectively and applying conceptual understanding to construct well-grounded arguments [4].

As a developing country, Indonesia is keen to promote students' soft skills, including argumentation, to prepare the younger generation for competitiveness. However, at this stage, Indonesian students' performance in this area remains insufficient. Some studies have found that Indonesian students' argumentation skills are unimpressive, with predominantly low levels (ranging from level 0 to 3) [11], [12]. Our previous research [13] also discovered that Indonesian students are unsatisfied with their ability to solve unfamiliar types of questions. This challenge reflects students' lack of argumentative skills, as evidenced by their apprehensive performances in international surveys such as PISA, TIMSS, and the Global Creativity Index (GCI). Therefore, promoting students' argumentation skills is a primary goal of the Indonesian government. For this reason, chemistry instruction should be designed to strengthen students' argumentation skills and deepen their mastery of chemistry concepts. Chemistry educators at the secondary and university levels are at the forefront of efforts to teach Indonesian students, aiming to develop their high-level thinking and skills in a holistic manner.

Pictorial-Based Learning (PcBL) & The role of visualisation in chemistry teaching

In recent decades, substantial studies have emerged, focusing on the advantages of utilizing visualizations encompassing graphics, drawings, animations, and simulations as a means to support the process of learning chemistry [14]. It fulfils instructional roles by capturing students' attention to particular content areas [15], illustrating both concrete and abstract details or processes [16], and demonstrating the operation of dynamic systems or the temporal evolution of scientific phenomena [17]. Visualisation plays a crucial role in educating students in the sciences [18]. Science, knowledge, and communication have all benefited greatly from the use of visualisation [18]. Therefore, it is inevitable that having knowledge of visualisation is the key to learning and understanding chemistry accordingly [19]. Many other types of media can be used to illustrate and convey scientific and chemical ideas, including but not limited to pictures, graphs, photographs, diagrams, and tables. Numerous studies provide credence to the claim that visuals are more memorable and effective for teaching scientific concepts and fostering the underlying cognitive processes of concept management, acquisition, and integration [20]. Students' cognitive growth and information-processing skills can be boosted by providing them with visually accurate representations of chemical concepts [21].

The ability of students to develop and use a model is an essential skill, as stated in the Next Generation Science Standards (NGSS) framework. The need to present models in chemistry and science teaching is primarily fulfilled through various media (physical or digital) to convey chemical concepts more easily. It describes, explores, and explains the abstract ideas of chemical behaviours [22]. However, utilising a model as an instructional approach is rare. Gaytan et al. have discussed the consent to consider the model as a supplement to content for students or as an instructional approach [23]. They presented works in biology and history that utilise models as scientific practice and suggested that the distinction between the two aspects could lead to significant consequences; therefore, they stressed that future research to explore this issue is required.

Chemistry teaching aims to promote students' understanding of chemistry and encourage them to learn the necessary 21st-century skills, including argumentation skills. The term argumentation skills can be traced back to the work of Toulmin since 1958, covering the ability to provide strong evidence to support the claim. It covers several key indicators: claim, data, warrant, backing, rebuttal, and qualifier [9].

In accordance with this study, some research employed graph-oriented methods with the assistance of computer tools to improve students' understanding and argumentation skills [24]. Another study utilised computer assistance to examine students' knowledge of socio-scientific issues [25]. In a more intense intervention, Crowell & Kuhn [10] worked for 3 years to improve students' argumentation skills. However, most of these studies were conducted on secondary and primary school students. Therefore, in this study, we followed up on these positive results at the university student level. Reflecting on the findings of their study, Evagorou & Osborne [8] suggested a further study to map students' argumentation skills from different backgrounds and perspectives. They also stressed using visualisation to promote students' understanding of science and how it works [26], which is compatible with argumentation skills.

When learning and teaching chemistry, visual representations like simulations and graphics are commonly used as mental scaffolding [17]. Langbeheim et al [27] utilised a pictorial representation to observe students' learning progress on the topic of matter and its properties. Some pictorial questions were also employed to reveal to students a scientific explanation of acid-base [28]. In this study, we applied Pictorial-based Learning (PcBL) in a general chemistry class and measured the profile of students' argumentation skills in each meeting. Students' deep understanding of chemistry was reflected in their responses to the integrative question type.

Our previous work [29] explored the potency of this approach for promoting students' conceptual change in chemical kinetics. Although we found that the advantage of PcBL students over Direct Instructional Teaching Method (DITM) students was only a small gap, the quality of PcBL students' answers was slightly higher than that of their counterparts. In addition, the pictorial approach has also been applied to uncover students' higher-order thinking skill levels [30] and their understanding of chemical kinetics [31]. Our previous review uncovered a significant contribution of visualisation in science teaching, including chemistry, but the number of studies focusing on this aspect is limited [32]. This approach also demonstrates long-term benefits in improving students' soft skills, including critical thinking, problem-solving, and argumentation [33].

Theoretical framework

Chemistry is the science that explains macroscopic phenomena (the real, tangible world) through microscopic reasoning (unobservable, abstract, and intangible) based on molecular chemical behaviour. For example, visually, students can observe that when water is placed in a freezer, freezing (ice) occurs, and the ice will float in water. This phenomenon is observable to the naked eye. What cannot be observed is the molecular behaviour that causes freezing: placing it in the freezer lowers the system's temperature, thereby reducing the kinetic energy of the water molecules. This situation slows the motion of water molecules, making their interactions more orderly, forming hydrogen bonds in a tetrahedral pattern, and creating a three-dimensional hexagonal network that leaves gaps between molecules, resulting in a lower density than water and causing it to float.

Johnstone's Triangle, or the triplet of chemical representation [34], highlights why science, including chemistry, is complicated for students. The root of the difficulty lies in the characteristics of science and the methods of teaching, which do not adequately take into account the nature of science itself. Johnstone introduced the concept of triplet representation [35]. Chemical concepts are communicated through three levels: (1) macroscopic or physically observable/tangible phenomena; (2) symbolic, involving symbols and reaction equations; and (3) sub-microscopic or particulate, which encompasses structural representations at the atomic and molecular levels.

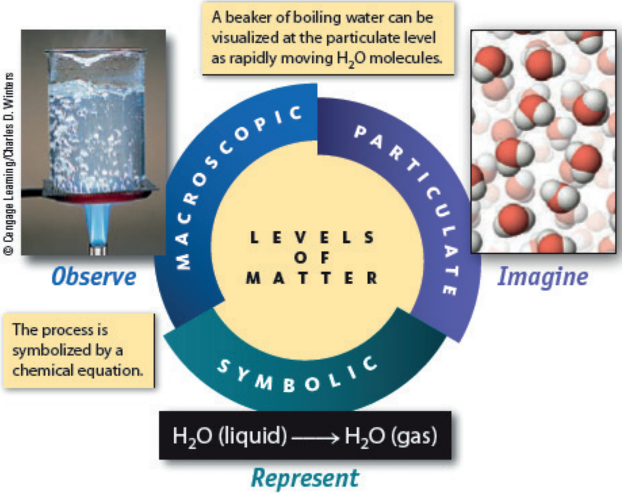

Figure 1. Representation of water (H_2O) at the three levels [36].

The chemical triple representation is exemplified by water (H_2O), as illustrated in Figure 1. At the macroscopic level, students perceive water in a glass, which can be ingested to alleviate thirst. At the microscopic level, they can only conceive of the innumerable water molecules (6.02×10^{23} H_2O molecules), each including two hydrogen atoms and one oxygen atom, with oxygen as the central atom and the two hydrogen atoms positioned as terminal atoms in a three-dimensional V configuration. Simultaneously, the symbolism of H_2O, encompassing phase state symbols (liquid/l, gas/g), enhances communication, particularly in textual contexts.

Representations in chemistry serve as instruments by which students, educators, and chemists engage with abstract chemical topics [37]. The ability to connect information, ideas, and transformations in each representation of a concept is a more meaningful indicator of understanding than manipulating symbolic notation [38], [39]. For example, many students, even those majoring in chemistry, can balance chemical equations by placing the correct coefficients and indices. However, understanding molecular behaviour or macro-scale phenomena represented by the equilibrium equation is a unique challenge for most chemistry students or undergraduates. To address this phenomenon, we utilise visualisation to help chemistry students learn more actively and meaningfully, and to serve as an assessment tool that reveals their deep understanding, based on Pictorial-Based Learning (PcBL).

The PcBL is expected to impact students' logical reasoning about the abstract nature of chemistry concepts for several reasons. Firstly, a visual model's demonstration of chemical behaviour will help students logically infer how and why chemical behaviours or reactions occur. Secondly, the dynamic representation will enhance the understanding of causal mechanisms in chemical processes by linking the three levels of chemical representations. Thirdly, reducing the cognitive burden by simplifying models leads to a focus on targeted concepts. At this stage, university students should already possess the ability to understand abstract concept entities [40]. Unfortunately, Bird [41] uncovered that most university-level chemistry students did not arrive at the formal operational stage. This lack of ability is rooted in the insufficient logical reasoning, which is also a robust predictor of students' performance in several chemistry courses [41].

The PcBL strategy in this study can be classified as a Brain-Based Educational Practice. Schunk [42] categorises Brain-based Educational Practice into several teaching strategies, including problem-based learning, simulations and role-playing, active discussions, graphics, and a favourable learning environment. According to multimedia learning theory, combining pictorial representation with verbal explanation contributes to a better learning outcome than verbal instruction alone [43]. Because of how our brains and eyes are wired, we absorb more information visually than in any other way [44]. The research indicates that linking the observable (macroscopic) realm of chemical phenomena to the imperceptible (particulate) domain of atoms and molecules improves student comprehension in chemistry [45].

The nature of chemical behaviour, explained by its sub-microscopic and particulate nature, requires modelling assistance to portray it in a concrete form. For this reason, students must be able to extract relevant information from visual representations in figures, graphs, and other forms. Chemistry teaching should be delivered optimally by considering the nature of chemical behaviour itself. In their work, Westbroek et al [46] described three prospective techniques to enhance substantive chemistry education: using pertinent situations, providing information on a necessary basis, and ensuring students perceive the significance of their contributions. Visual representations reduce the students' cognitive capacity, which is limited according to the cognitive load theory [47], [48]. Taking this into account, utilising visualisation is a form of teaching chemistry on a student-necessity basis.

Students' activity in PcBL is expected to train their argumentation skills. Science, including chemistry concepts, is constructed from a scientific process involving observation, data collection, and conclusion. These constructions are justified by theories explaining why the observable facts occur. For example, a series of observations led to a relationship between temperature and gas volume at constant pressure (Charles's Law). The phenomenon and other gas laws are theoretically explained by the kinetic molecular theory. In building theories to explain observable facts, events, and other phenomena, agreement and disagreement often exist [49]. The incidents of disagreement, conflicting opinions, and challenges to ideas mostly occur more often than general agreement [50], [51]. Therefore, chemistry students should exhibit strong argumentation skills.

Scientific argumentation is a skill demanding sufficient reasoning in conjunction with other inquiry-thinking processes [52]. Studies in this area involving chemistry students as prospective chemistry teachers are limited [53]. Scientific reasoning involves cognitive processes that facilitate creating and testing hypotheses, which are crucial components of scientific undertakings [54]. These cognitive processes encompass formal logic, such as probabilistic logic, as well as non-formal processes, including model-based reasoning[55] and analogical reasoning [56].

Scientific argumentation has been essential to mastering scientific concepts [57] due to its significant support for cognitive skills and undeniable function in 21st-century skills [58]. Students will automatically process and delve into their more profound understanding by presenting the key indicators of argumentation skills [59].

Although the vital pivotal role of argumentation skills has been acknowledged worldwide, limited effort has been made to employ an instructional approach specifically to train them intentionally [60]. This approach is derived from characteristic chemistry concepts that embrace the role of models and modelling, particularly visualisation. Therefore, in this study, we utilised a specific chemistry teaching approach, PcBL, to build students' skills and understanding of chemistry. The term 'understanding' has several definitions in the education community. In Bloom's cognitive taxonomy, understanding is a second level of taxonomy, representing a low mastery level. In this paper, we refer to the meaning of 'understanding' in line with several key aspects of conceptual understanding, including fundamental/basic understanding, applying knowledge, answering questions, and explaining concepts [61].

Research aims

The objectives of this research are to measure and describe: (1) the profile of chemistry students' argumentation skills levels after experiencing PcBL in the topic of Solubility & Intermolecular Forces (SIF), Gas Laws (GL), Kinetic Molecular Theory (KMT), and Thermochemistry (Thc), (2) the progress of students' argumentation skills levels during 1 teaching term using PcBL across the four topics, (3) students' understanding across the four topics after experiencing PcBL, and (4) the correlation between students' understanding and their argumentation skills levels.

2. METHOD

This study employed a single-group experimental design and involved 35 first-year students of chemistry education at Universitas Negeri Malang, aged 19 to 21 years old. The study was conducted over one semester in the 2022/2023 academic year, focusing on Basic Chemistry 2, which covered three topics: Solubility & Intermolecular Forces, gas laws, and thermochemistry. The group of students participating in this study was a bilingual class. In our department, among the eight classes in the total student intake each year, several eligible students are assigned to a single class as bilingual students. The teaching process in this class occurs in both Indonesian and English. Therefore, having two equal experimental and comparison groups is not feasible due to the department's lack of two comparable classes. The primary requirement for this class is English proficiency, which is assessed on the first day at the university. The students completed the Basic Chemistry 1 course before embarking on this study. In Basic Chemistry 1, students learned about matter and measurement, stoichiometry, atomic structure, and chemical bonding.

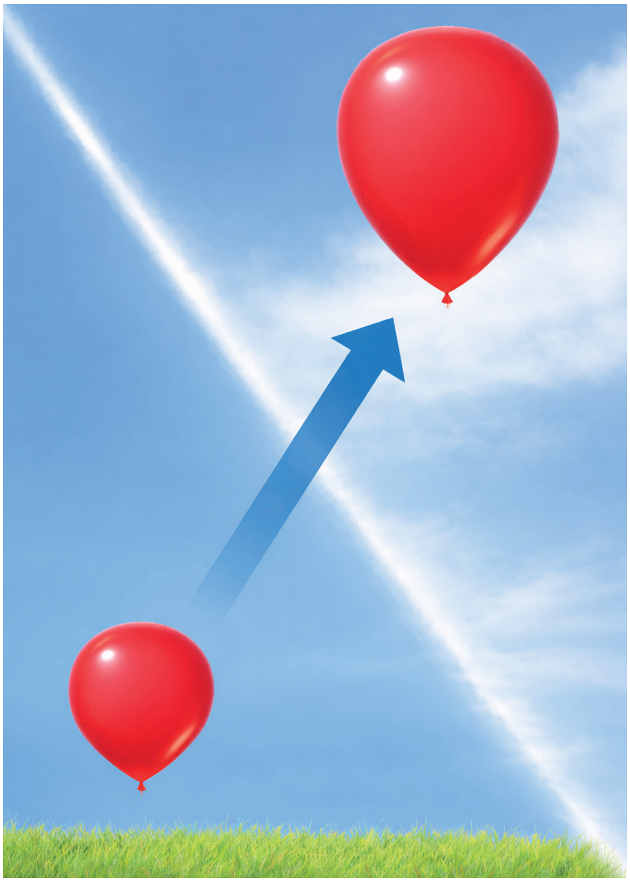

Figure 2. Pictorial trigger for Boyle's Law

PcBL syntax

The PcBL strategy is implemented in the general chemistry class through the following steps: opening, pictorial trigger, concept exploration and sharing, verification and closure. Let's explain these steps in the teaching of Gas Laws. At the *opening* stage, the lecturer provides a brief explanation of the learning aims and a brief overview of the Gas Laws, without delving into the concepts. Next (*pictorial trigger*), the image depicting gas behaviour is presented (Figure 2). These pictures served as a cognitive trigger for students to understand the relationship between volume (V) and pressure (P) as explained by Boyle's Law. How does the volume of the balloon increase with the higher altitude in the atmosphere? Students should also determine whether atmospheric pressure increases or decreases with increasing altitude. At this stage, students should individually extract information from the Figure and relate it to gas behaviour. In the next step (*concept exploration and sharing*), students work in pairs to discuss and share their interpretations of the figure and its relationship to the concept. The discussion is followed by the lecturer leading it classically. The students talked about what they learnt from the picture interactively. The lecture concludes the class after all the concepts have been discussed in accordance with the scientific understanding (*verification and closure*).

Instrument & Data Collection

Students' argumentation skills were measured at the end of each topic using 3 instruments, including the Argumentation Test of Solubility & Intermolecular Forces (SIF), Gas Laws (GL), Kinetic Molecular Theory (KMT), and Thermochemistry (Thc). Each instrument was administered at the end of the teaching for each topic. Each topic was carried out for 3-4 meetings. Toulmin's Argument Pattern (TAP), comprising claims, data, warrants, backing, qualifiers, and rebuttals, is employed in this study [62] to assess students' argumentation skills. A claim is a public statement for general acceptance, such as *it is correct, I have no idea, or it is incorrect.* Data are evidence that supports a claim, for example, *it is correct* (**claim**) because *the frequency of collision increases the reaction rate* (**data**). A warrant describes the correlation between the claim and the data. For example, *the reaction will be faster in a smaller area (volume).* Backing is a generalisation that clarifies the body of experience utilised to validate the believability of the argumentative approach employed in a specific instance. For instance, *according to collision theory, increasing collision frequency increases the amount of energy produced to reach the activation energy.* A rebuttal is an exceptional situation that may undermine the strength of a supporting argument. Meanwhile, a qualifier refers to a statement that denotes the confidence level that may be attributed to a conclusion based on the supporting arguments provided.

The authors developed all the argumentation skill questions. Subsequently, colleagues, organic and physical chemists responsible for teaching final-year students in the chemistry department, reviewed the prototype questions, resulting in minor adjustments to several questions. Meanwhile, students' understanding was evaluated at the end of the semester using a multiple-choice instrument type (instrument available on request). The instrument is named Test of Chemistry Students' Understanding (TCSU) for simplification. The test was constructed collectively by the Basic Chemistry Team Teaching and utilised to evaluate all students taking Basic Chemistry (8 classes in total) within the Chemistry department.

Data Analysis

The detailed frameworks for categorising the level of students' argumentation skills are employed in the procedure from Cetin [62], as provided in Table 1. Content analysis procedures, adopted from Lundman et al and Kleinheksel et al [63], [64] were employed to assign the level of students' argumentation skills: organisation, coding, interpretation (initial categorisation), peer debriefing, and final categorisation. At the organisation stage, students' answers to the argumentation test were grouped into two groups (correct and incorrect answers). The incorrect answers or those left empty on the answer sheet are categorised as Level 0 of argumentation skills (L0AS). The correct answers are further sent to the coding stage. During the coding stage, students' answers are stored based on the similarity of their conceptual points of view. For example, in the GL question, those related to the change in temperature with the volume change are grouped in the same compartment. In the interpretation stage, all the answers were assigned to the relevant argumentation level (Levels 1 – 5). The next stage, peer debriefing, is a recheck and discussion with all the team members to ensure that the assigned level is acceptable. At the final categorisation, strong agreement was obtained, and the final categories of students' argumentation levels were reformed.

Table 1. Framework for assessing students' argumentation skills [62].

Level	Description
Level 1 (L1AS)	Claim only
Level 2 (L2AS)	Claim, data (evidence supporting the claim) and/or warrant (relationship between claim and data)
Level 3 (L3AS)	Claim, data/warrant, backing or qualifier
Level 4 (L4AS)	Claim, data/warrant, backing and qualifier

Students' understanding is classified based on the percentage of obtained scores, as displayed in Table 2.

The categorisation of students' understanding, as displayed in Table 2, is built upon the procedure for determining the course final grade in some Indonesian universities. The correlation between students' knowledge of chemistry and the level of their argumentation skills was measured using *the product-moment correlation*. As aforementioned, students' understanding of chemistry is obtained from their scores at TCSU.

Table 2. The classification of students' understanding

Score	Category
85 - 100	High
70-84	Moderate
55-69	Weak
< 54	Poor

3. RESULTS AND DISCUSSION

Profile of Students' Argumentation Skills: Solubility & Intermolecular Forces (SIF)

Solubility & intermolecular forces have been taught at secondary and university levels in many countries. Knowledge regarding intermolecular forces is essential for students to predict material properties correctly [65], including chemical & physical properties and bioactivity [66], [67]. This topic is challenging for students due to the confusion of terminology between intramolecular and intermolecular forces [68]. Robust understanding in this area is essential because it can be utilised to explain molecular interaction mechanisms (how and why) [66]. However, based on our searching so far, the number of studies concerning solubility & intermolecular forces mainly how the teaching of the topic influences students' argumentation skills, is unfound.

In this study, students' argumentation skills related to solubility & intermolecular forces were assessed using the following question. Here is the question: "*At 25°C, the solubility of benzoic acid ($HC_7H_5O_2$) in water is lower than its solubility in benzene. Assess whether the statement is correct or incorrect.* (*Hint: Benzoic acid produces a dimer with benzene*).

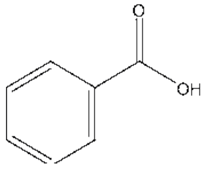

Figure 3. Structure of Benzoic Acid

This question is designed to assess students' scientific understanding of solubility principles, specifically the scientific argumentation they will provide to support their answers. Whether students can correctly mention the solubility values of benzoic acid in water (0.34 g/100 mL) and in Benzene (C_6H_6), 10.0 g/100 mL, is not the primary concern; how do students provide a scientific argument instead? The hint regarding dimer formation is offered to stimulate students' ideas about the dimer structure and its relationship to the molecule's polarity. Students with low scientific reasoning may simply apply the rule of like dissolves like by considering that the polarity of water is greater than that of benzene. By acknowledging that benzoic acid is also polar, they may assume that its solubility in water will be higher. They could ignore the monomeric structure of the acid.

The monomeric structure of benzoic acid (Figure 3) will form a dimer of benzoic acid with equivalent H-bonds [69]. Dimeric structures endure in low-polarity solutions. However, their stability is primarily contingent upon the solvent [70]. Therefore, this dimerisation should be a clue for students to predict the solubility of the compound in water and benzene by considering the polarity of the formed dimer. This scientific reasoning is seemingly in consideration of some students with scientific argumentation, as presented in Table 3.

Students mostly recognised that the solubility of benzoic acid in benzene is higher than its solubility in water. This phenomenon is confirmed by the majority of students who mostly provided the claim 'the statement is correct'. However, the number of students who follow the claim and data with relevant warrants is equal to those without warrants. Many students with Level 2 Argumentation Skill (L2AS) provided claims and data without warrants, backing, and qualifiers. However, some followed this with a warrant that the structure of benzoic acid facilitates dimer formation, leading to a decrease in polarity. Therefore, its solubility in a non-polar solvent (benzene) is higher than that of water, which is more polar.

Students with Level 3 Argumentation Skill (L3AS) demonstrated concept mastery comparable to that of L2AS students, except that they classified their answers as claim, data, warrant, and qualifier in a proper manner. Only a single student demonstrated an outstanding Level 4 Argumentation Skill (L4AS). The student provided a robust scientific understanding and argument with a good logical order. The student began with the formation of a dimer due to the intermolecular bonding of the benzoic acid molecules (claim). The warrant

Level 2

Claim	Data	Warrant
The statement is correct.	• The solubility of benzoic acid is distributed between two phases according to an equilibrium equation. • Benzoic acid is hardly soluble in water but in ethanol, chloroform, and ether. • Benzoic acid is a weak acid. • Because at the same temperature, the solubility of benzoic acid in organic solvents (11 g/100 mL) is higher than its solubility in water (0,34 g/100 mL) • The solubility of benzoic acid in water is 0.34 g/100 mL • The solubility of benzoic acid in benzene is higher with 10.0 g/100 mL • Benzoic acid will form dimer in benzene	
	Benzoic acid is soluble in benzene, forming hydrogen bonds between molecules.	It leads to the formation of dimer.
	Benzoic acid is soluble in benzene, forming a dimer.	The solubility of benzoic acid in benzene is higher than in water.
	• The solubility of benzoic acid in water is lower than 1 • The solubility of benzoic acid in benzene ranges from 1 – 10	• Benzoic acid is easily soluble in water • Benzoic acid can also be soluble in other organic solvents
	Benzoic acid will form dimer in benzene due to the hydrogen bonding	• Benzoic acid is easily soluble in benzene • Benzoic acid is hardly soluble in water

Level 3

Claim	Data	Warrant	Qualifier
The statement is correct.	Benzoic acid has a non-polar outer site	It forms a dimer that is insoluble in water	The dimer could lead to the insolubility of benzoic acid in water
	• Benzoic acid is hardly soluble in water but is greatly soluble in chloroform, ether, and ethanol. • Benzoic acid is a weak carboxylate aromatic acid.		Benzoic acid is soluble in benzene because both are non-polar.
	• The solubility of benzoic acid will be distributed between two phases, which refers to the equilibrium equation. • Benzoic acid is soluble in benzene and forms hydrogen bonding	The hydrogen bonding leads to the formation of dimer	Therefore, benzoic acid is more soluble in benzene than in water or other non-organic solvents
	Both benzoic acid and benzene are non-polar	Benzoic acid is soluble in benzene and forms hydrogen bonding	The hydrogen bonding could lead to the formation of a dimer
	• The solubility of benzoic acid in water is 0,34 g/100 mL • The solubility of benzoic acid in benzene is 10,0 g/100 mL (higher)		• Benzoic acid is hardly soluble in water • Benzoic acid forms a dimer with benzene • Hydrocarbon compounds are mostly non-polar
	Benzoic acid is soluble in benzene and forms hydrogen bonding, leading to a dimer formation.		The dimer is the unification of two identical molecules.
	Benzoic acid is more soluble in benzene due to the hydrogen bonding	The hydrogen bonding leads to the formation of dimer	Benzoic acid is insoluble in water because the carboxylic group is polar, but most parts of the benzoic acid molecule are non-polar

Level 4

Claim	Data	Warrant	Backing	Qualifier
The statement is correct.	Benzoic acid will form dimer due to the intermolecular bonding	The solubility of benzoic acid in benzene is higher than its solubility in water	Solubility will be higher if the polarity between the two molecules is similar	The dimers of Benzoic acid and benzene are both non-polar, while water is polar

Table 3. Examples of Argumentation Skills Levels for SIF

that the solubility of benzoic acid in benzene is higher than in water was followed by the backing that solubility will be higher if the polarity between the two molecules is similar. The qualifier that "the dimer of Benzoic acid and Benzene is both non-polar, while water is polar" is assertive for the L4AS quality.

All in all, those students always provide at least follow-up data to support their claim that the solubility of benzoic acid in water is lower than its solubility in benzene. This study provided supportive evidence that the use of PcBL positively contributed to the formation of students' scientific argumentation in Solubility and Intermolecular Forces. The previous study [71] found that students' understanding of intermolecular forces could be fostered with problem-based learning and reduced the topic's unscientific understanding of incidents.

Profile of Student's Argumentation Skills: Gas Laws

In Indonesian universities, Gas Laws are covered in introductory chemistry and physical chemistry courses. The works of Robert Boyle, Jacque Charles, and Amedeo Avogadro are recognised as the 3 historical milestones of gas laws introduced in both courses. In this study, students' argumentation skills related to gas laws were assessed using the following question focusing on the relationship of volume, temperature and moles of gases. As per the previous topic, using gas laws to assess students' argumentation skills has not been found. The following statement is the question *in italics*. *After the appropriate adjustments have been made to the initial gas sample maintained at a pressure of 1.0 atm, demonstrate the approximate level of the movable piston in Figures 3 (a) and (b).* This question aims to measure students' understanding of applying the Gas Laws from a picture of a movable piston.

This typical question is uncommon in the assessment procedures for basic chemistry class assessment in many Indonesian universities. The questions are mostly presented on an algorithmic basis, in which students are required to calculate one of the variables (pressure/P, volume/V, or temperature/T) with two other known variables. Students can simply substitute all the numerical values into the gas laws formulas and do mathematical operations. Therefore, it is often the case that in some chemistry topics, including chemical kinetics [30], [31], limiting reactants [72], stoichiometry [73], basic quantum [74] students can provide a correct mathematical calculation without fully understanding the conceptual meaning of the formula.

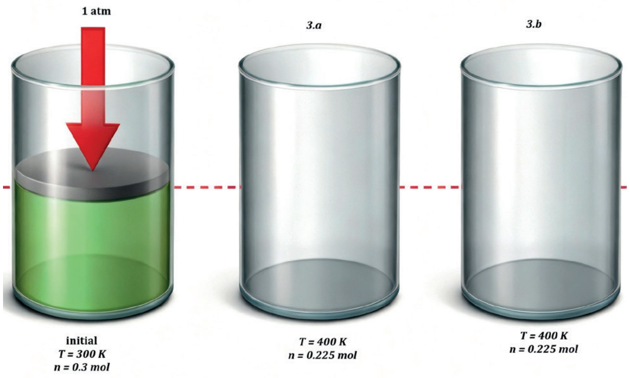

Figure 4. A movable piston

Students with robust scientific understanding firmly recognise the relationship between the temperature of the gas system and the mole. They addressed that the temperature increases 1.3 times while the mole decreases with the same value, leading to a constant volume of V1 to VA. Meanwhile, for the V1 to VB, both variables decrease by 1.5 times for temperature and 1.3 times for the mole. Therefore, they correctly predicted that the VB < V1. In this circumstance, the question was not intended to ask students to provide an exact numerical value of the change in volume due to the changes in the two variables. For this reason, the numerical values provided by students to support their answers are not taken into account for grading procedures. However, the ultimate measures are the scientific logic regarding the change in volume, whether an increase, a decrease or a constant and the argument for backing those. The previous study on Gas laws found that students' success in answering Gas laws questions depends on 3 factors, including number format, volume unit, and temperature unit [75].

As in the previous topic, most students correctly identified the claim and the data. They all understood the relationship between pressure, volume, and moles in gas behaviour. In this topic, all L2AS students supported their claim with a warrant, including that the volume of gases increases with temperature, decreases with temperature, and decreases with the number of moles. The most intriguing backing from L3AS is that Avogadro's Law is inapplicable, implying a cautious assessment of the effect of the two variables (temperature and moles). The students considered that (Figure 4.a) the increase in temperature (300 – 400 K) increases the volume, while the decrease in mole (0.3 – 0.225 mol) decreases the volume. The contradictory effect leads students to conclude that the initial volume (VI) tends not to change significantly (VA). As with the previous topic, L4AS students demonstrated a better order of logical reasoning, from

Level 2		
Claim	**Data**	**Warrant**
• VA = VI • VB = ½ VI • VB decreases • The figure describes the temperature and the number of moles of the gases	• VI = 90 R; VA = 90 R; VB = 45 R • VA = VI; VB = ½ VI • VA = 8.96 L; VB = 4.48 L • VA = 90 R; VB = 45 R	• Due to the difference in temperature and mole with the constant pressure of 1 atm • The volume of gases increases with the increase in temperature • The volume of gases decreases with the decrease in temperature • The volume of gases decreases with the decrease in moles

Level 3			
Claim	**Data**	**Warrant**	**Backing**
• VB decreases • VB decreases as predicted by Charles's and Avogadro's Laws • The volume of gases increases with the increase in temperature	• VI = 90 R • VA = 90 R • VB = 45 R	• The volume of gases increases with the increase in temperature • The volume of gases decreases with the decrease in temperature • The volume of gases decreases with the decrease in moles	• Applying Charles's Law due to the constant piston pressure • Avogadro's Law is not applicable • Charles's, Gay-Lussac's and Avogadro's laws • Applying Charles's Law due to the constant piston pressure

Level 4				
Claim	**Data**	**Warrant**	**Backing**	**Qualifier**
• VB decreases • VA = VI • VB ≠ VA • VA > VB	• VA = VI; VB = ½ VI • VI = 90 R; VA = 90 R; VB = 45 R • TA is higher • VI = 7.38; VA = 7.38; VB = 3.69	• No change in the VA, while the VB decreases by half of the VI • The volume of gases increases with the increase in temperature • The volume of gases decreases with the decrease in temperature • In this case, the temperature affects the volume	• Following Avogadro's, Charles's, and Gay-Lussac's laws • Following Charles's and Avogadro's laws	• In many circumstances, the volume of gases increases with the increase in temperature, and vice versa. • The volume of gases mostly decreases with a decrease in moles. • According to Charles's Law, at a constant pressure, the volume of gas is directly proportional to its temperature. • According to Avogadro's Law, at constant pressure and temperature, the volume of gas is directly proportional to its moles. • The volume of gases mainly decreases with a decrease in temperature • According to Charles's and Gay-Lussac's Laws, at constant pressure, the volume of gas is directly proportional to its temperature

Table 4. Examples of Argumentation Skills Levels for GL

the possible change of the volume in two conditions to its relation to the gas laws' behaviours.

Profile of Students' Argumentation Skills: Kinetic Molecular Theory (KMT)

In this study, the question for the Kinetic Molecular Theory (KMT) of gases is represented by the root mean square velocity. It represents the measure of gas-particle average speed. In most Indonesian universities, this topic is hardly covered in basic chemistry courses but in physical chemistry. However, this concept is provided in many general chemistry textbooks, which are the most common references for basic chemistry courses.

Students' argumentation skills related to the Kinetic Molecular Theory of gases were assessed using the question below. *At 65°C, the O_2 molecule moves 3.3 times faster than the UF_6 molecule. Identify whether the statement is correct or incorrect. Provide your scientific arguments.*

$$U_{ark} = \sqrt{\frac{3RT}{M}} \quad \textit{With M is molar mass.}$$

Level 2				
Claim	**Data**	**Warrant**		
Correct statement	• U_{ark} O_2 16 m/s; U_{ark} UF_6 4.89 m/s • U_{ark} O_2 1.62 x 10^3 m/s; U_{ark} UF_6 1.52 x 10^5 m/s • U_{ark} O_2 2.6 x 10^3 m/s; U_{ark} UF_6 0.23 x 10^5 m/s • U_{ark} O_2 263.44 m/s; U_{ark} UF_6 23.9 m/s • U_{ark} O_2 1.16 m/s; U_{ark} UF_6 0.468 m/s	• The molar mass of O_2 is lower than that of UF_6 molecules; therefore, the former one is 3,3 times faster • The higher the temperature, the faster the gas molecules • The higher the molar mass of gas molecules, the slower its movement		
Level 3				
Claim	**Data**	**Warrant**	**Backing**	**Qualifier**
Correct statement	• U_{ark} O_2 1.16 m/s; U_{ark} UF_6 0.49 m/s • U_{ark} O_2 : U_{ark} UF_6 = 3.3 : 1 • U_{ark} O_2 3.3 m/s; U_{ark} UF_6 0.23 m/s • U_{ark} O_2 513 m/s; U_{ark} UF_6 154 m/s • U_{ark} O_2 16.2 m/s; U_{ark} UF_6 4.9 m/s • The molar mass of O_2 is 36 g/mole, and UF_6 is 352 g/mole	• The molecule of gas O_2 moves 3.3 times faster than the molecule of gas UF_6 • The calculation using the RMS speed equation confirms the ratio • The higher the molecular mass, the lower the U_{ark} value	• The velocity of gas molecules is determined by the gas constant, temperature, and molar mass • According to the kinetic molecular theory of gases, the molecular speed of gases is affected by the temperature, in which the higher the temperature, the higher the kinetic energy, leading to a higher molecular speed	
Correct statement	• U_{ark} O_2 1.16 m/s; U_{ark} UF_6 0.49 m/s • U_{ark} O_2 : U_{ark} UF_6 = 3.3 : 1 • U_{ark} O_2 3.3 m/s; U_{ark} UF_6 0.23 m/s • U_{ark} O_2 513 m/s; U_{ark} UF_6 154 m/s • U_{ark} O_2 16.2 m/s; U_{ark} UF_6 4.9 m/s • The molar mass of O_2 is 36 g/mole, and UF_6 is 352 g/mole	• The molecule of gas O_2 moves 3.3 times faster than the molecule of gas UF_6 • The calculation using the RMS speed equation confirms the ratio • The higher the molecular mass, the lower the Uark value		• At the same temperature, a gas with a lower molar mass will have a higher molecular speed. • The molecular speed of gases is inversely proportional to their molar mass.
Level 4				
Claim	**Data**	**Warrant**	**Backing**	**Qualifier**
Correct statement	• U_{ark} O_2 1.6 m/s; U_{ark} UF_6 0.479 m/s • The kinetic energy produced in the O_2 molecules is higher than that of the UF_6 • U_{ark} O_2 : U_{ark} ; UF_6 = 3.3 : 1 • The molecular speed of gas molecules is inversely proportional to the molar mass.	• The molecular speed of O_2 molecules is higher due to its lower molar mass compared to the molar mass of UF_6 • At the same temperature (65°C), The molecular speed of O_2 is 3.3 times higher than the speed of UF_6 molecules. • At the same temperature, the higher the molar mass, the lower the molecular speed	• The calculation using the RMS speed equation confirms the ratio of molecular speed between O_2 and UF_6 molecules. • The difference in molar mass • The phenomenon is relevant to the kinetic molecular theory of gases • Graham's Law of Effusion	• The equation shows that the molar mass (M) is inversely proportional to the Uark • At the same temperature, the higher the molar mass, the molecular speed tends to be lower. • At the same temperature and pressure, the diffusion and effusion of gases are inversely proportional to the molar mass.

Table 5. Examples of Argumentation Skills Levels for KMT

In this question, students are required to figure out that the Root-mean-square velocity of a gas is directly proportional to the square root of its temperature, measured in kelvins. Since the variable *M* is present in the denominator, it may be inferred that the greater the weight of the gas, the slower the movement of its molecules. Acknowledging the O_2 and UF_6 molar mass ratio, they should understand that the statement is correct.

All the students with L2AS in this topic provided a warrant regarding the effect of molar mass on the molecular speed of those gases. Meanwhile, those with L3AS incorporated their warrant with the backing related to the relationship between temperature and molar mass and the gases’ molecular speed. Students with L4AS even completed their qualifier regarding gas diffusion and effusion behaviours.

Profile of Students’ Argumentation Skills: Thermochemistry (Thc)

Thermochemistry is a quite familiar topic for chemistry students in Indonesia. Their exposure to the topic has been experienced since secondary school, first-year university and the following years in some advanced chemistry courses such as thermodynamics, physical chemistry and others. Considering that the topic is a basis for understanding other concepts, such as thermodynamics, is understandable. Studies on the topic of thermochemistry related to students’ understanding and unscientific understanding have been carried out in previous research [76].

Students’ argumentation skills related to thermochemistry were assessed using the following questions, particularly in the concept of Hess law.

Calculate the ΔH° for the following reaction (use data from a table of thermodynamic data)

$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

$2Na(s) + CO_2(g) \rightarrow Na_2O(s) + CO(g)$

Please state whether the following statement *is correct or incorrect: “An excellent way to put out a sodium fire is with a water or carbon dioxide fire extinguisher.” Identify whether the statement is correct or incorrect. Explain your answer.*

Table 6 demonstrates students’ strong knowledge of calculating the enthalpy change for the chemical reaction presented in the question. Solving questions related to Hess Laws requires mathematical operation ability, which Indonesian students are primarily good at [31]. For this reason, the question was not emphasised in the calculation of the Hess Law. Students with L2AS focused on the classification of fire extinguishers to support their belief that, as class D fire, water or carbon dioxide are unsuitable for sodium fire. Meanwhile, those with L3AS followed up their warrant with a qualifier regarding the reactivity of sodium to water, leading to an explosion in contact. Meanwhile, L4AS students incorporated their argument, supported by evidence that the energy released by the reaction between sodium and water.

Progress of Students’ Argumentation Skills

The level of students’ argumentation skills was evaluated on every topic. With this procedure, the growth of students’ argumentation skills was monitored. The descriptions of. Figure 4 shows that in the first topic, Solubility & Intermolecular Forces, although no L1AS was observed, students’ argumentation skills generally fall in the weak category. This phenomenon is derived from the fact that most students demonstrated L0AS with 13 students (highest), followed by the L2AS and L3AS in order. Meanwhile, only 1 student demonstrated level 4 (L4AS) in this topic. This ensures that most students’ argumentation skills in the SIF topic are mainly at the lower level, with a significant drop at L4AS.

A different trend emerges for the Gas Laws (GL), recording the highest number of students with L4AS over the topics, reaching 10. The number of students with L0AS also dropped significantly, with only 5 students. This trend indicates a shift in students’ argumentation skills to higher levels, with L3AS leading the count.

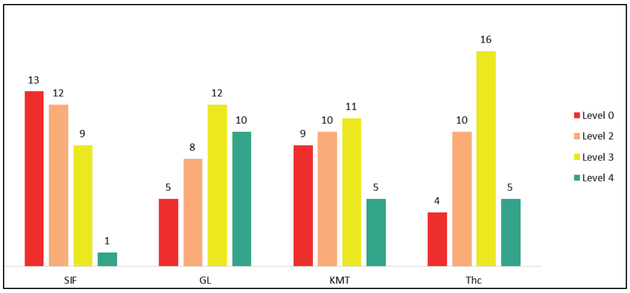

Figure 5. The progress of students’ argumentation skills level each topic (SIF: Solubility & Intermolecular Forces, GL: Gas Laws, KMT: Kinetic molecular Theory, Thc: Thermochemistry)

A more variative distribution of students’ argumentation skills is demonstrated for KMT. The highest argumentation level is found at L3AS with 11 students, while L2AS is slightly behind with 10 students. L0AS also obtains a relatively high number of 9 students. Meanwhile, the number of L4AS students was slightly higher for the second topic but still higher than the first.

The level of argumentation skills in thermochemistry (Thc) exhibits a unique trend, peaking at the L3AS with 16 students. As the first three topics, L3AS also dominated the incident of argumentation level in thermochemistry. With the majority of students’ argumentation level concentrated in Level 3, a sharp decline at the lower and higher levels (L2AS and L4AS) is observed. All in all, Figure 5 reveals that L3AS consistently holds the highest number across the four topics. Meanwhile,

Level 2				
Claim	**Data**	**Warrant**		
Incorrect statement	• ΔH1= -832 kJ/mol • ΔH2= -368 kJ/mol • ΔH3= -133 kJ/mol • For solid metals such as magnesium, aluminium, sodium, potassium, and others, dry powder and sand are recommended	• Sodium fire is classified as Class D fire in which water and regular fire extinguishers involving combustible reactive metals should not be applied; instead, dry powder is recommended. • Water is used as an extinguisher for non-metals such as wood, paper, and plastic. Meanwhile, CO_2 is used for flammable liquids and high-voltage electricity. • Sodium forms flammable hydrogen and NaOH when in contact with water, so it is not suggested that the fire be extinguished with sodium.		
Level 3				
Claim	**Data**	**Warrant**	**Qualifier**	
Incorrect statement	• ΔH1 = -831.8 kJ/mol • ΔH2 = -368.4 kJ/mol • ΔH3 = -132.9 kJ/mol • The chemical equations tell us that the reaction between sodium and water or CO_2 produces gases.	• Sodium fire is classified as Class D fire in which water and regular fire extinguishers involving combustible reactive metals should not be applied; instead, dry powder is recommended. • When sodium is in contact with water or carbon dioxide, an exothermic reaction with enough energy/heat to spontaneously burn H2 gas and ignite an explosion.	• Sodium is reactive to water and explosive; meanwhile, CO_2 will spread the fire quickly. • The contact between sodium and water will enhance the burning instead of extinguishing it. • Water is used as an extinguisher for non-metals such as wood, paper, and plastic. Meanwhile, CO_2 is used for flammable liquid and high-voltage electricity. • Carbon dioxide extinguishers are suitable for use on Class B and Class C fires.	
Level 4				
Claim	**Data**	**Warrant**	**Backing**	**Qualifier**
Incorrect statement	• ΔH1 = -831.78 kJ/mol • ΔH2 = -367.6 kJ/mol • ΔH3 = -132.89 kJ/mol	Water extinguishers (Class A) are used for non-metal solid fires such as paper, cloth, wood, and rubber. Meanwhile, Carbon Dioxide (CO2) is used for flammable liquids (class B) and electrical equipment (Class C).	• Most alkali metals, such as sodium, react with water exothermically. So, a small piece of it can explode. • The reaction between sodium metal and water generates a lot of heat (exothermic) because the hydrogen gas formed during the reaction will ignite and cause a small explosion. Regarding the energy released, the reaction between sodium and water is also quite high.	The reaction produces caustic soda (sodium hydroxide) and flammable hydrogen gas in this case. Therefore, if a metal fire is extinguished with water or carbon dioxide, it can cause a steam explosion that can spread over a wider area.

Table 6. Examples of Argumentation Skills Levels for Thc

the SIF showed the highest L0AS, indicating that many students were unable to provide the expected answer on this topic.

Figure 5 also describes the progress of students' argumentation levels on each topic. The figure shows that L2AS slightly dropped over topics, while L3AS substantially improved. This implies that students' argumentation levels increase over time. An interesting phenomenon is observed for the L4AS. The number of students showing for this level was initially very low, with only 1 student (SIF). However, the number of students showing this level gradually increased over the meetings and topics. However, the highest number was shown on the Gas Laws, the second topic among the four. Based on this data, it is more likely that students' argumentation skills will reach a peak in this area.

The outcomes of this study demonstrate a significantly higher argumentation level than the previous findings in Indonesian universities [77], [78] that mostly concentrated on Level 2. However, comparing the findings of this study with those of the two studies should be approached cautiously due to the differing research designs between them. Additionally, the nature of each topic can also impact students' argumentation skills. A topic that is considered challenging may lead to suboptimal argumentative skills among students, and vice versa. Despite these limitations, this study positively enhanced students' argumentation skills by providing them with a challenging exercise. Cox & Gulacar [79] offered regular and irregular tasks for two different groups in the Gas Laws teaching and found better performances for those with irregular tasks. To sum up, this study demonstrates similar results to the previous findings, accomplishing positive evidence in improving students' argumentation skills using an integrated instructional approach [80], Argument-Driven Inquiry (ADI)[81], laboratory-based course [82] and others.

Student's Understanding of Basic Chemistry

Students' understanding of chemistry after experiencing PcBL is retrieved by the score of their answer to the TCSU. The test consisted of 30 multiple-choice questions covering all four topics, as well as additional topics not included in the argumentative questions, such as matter and measurement, stoichiometry. Students' scores were converted to a maximum of 100 if they answered all the questions correctly. The TCSU was used as the basis for grading students' achievements in the basic chemistry class with the following criteria: >85 for A, 80–84 for A^-, 75–79 for B^+, 70-74 for B, 65-69 for C^+, 60-64 for C, 55-59 for D, and <55 for E. A grade of C is the minimum requirement for passing the course. The question was in the Indonesian language because the TCSU was also applied to other non-bilingual classes. An example of a translated question is provided in Figure 6. The question is designed to assess students' mastery of applying gas laws.

A container has a volume of 2.10 L, containing a gas with a mass of 4.65 g at a pressure of 1.00 atm and a temperature of 27.0 °C. What is the molar mass of the gas?

A. 55.14 g/mol
B. 54.6 g/mol
C. 49.60 g/mol
D. 48.9 g/mol
E. 11.10 g/mol

Figure 6. Example of a question in the TCSU instrument

Table 7 shows the distribution of students' numbers based on the score in answering the TCSU and corresponding performance categories. Notably, none of the students recorded the most expected performance (85-100). However, the number of students in the moderate and weak categories is equal. On average, the students' scores were 63.4, falling into the *weak* category. Although none of the students reached the *robust* category, a substantial portion (40%) demonstrated a quite moderate understanding, with scores over 70. As additional information, compared with the other 7 classes of first-year chemistry students who took the same test at the university, taught using a non-PcBL approach, this class performed better. With only 7 PcBL students scoring in the poor category, this is a worthwhile exercise in chemistry instruction.

Table 7. Examples of Argumentation Skills Levels for Thc

Score	Number of students	Category
85 - 100	0	High
70-84	14	Moderate
55-69	14	Weak
< 54	7	Poor

This finding is positive evidence that the PcBL is a potential teaching approach for improving students' understanding. In our previous research employing this approach [29], students performed better in answering chemical kinetics questions than non-PcBL students. In another study, using the eChem tool to link chemical concepts and representations can promote chemistry students' understanding [83]. Visual model mastery is even considered a predictive tool of students' general chemistry examination grades [19]. To sum up, several studies have confirmed the positive impact of visualisation in fostering students' understanding of many chemistry topics, including stereochemistry [84], electrochemistry [14], [85], chemical reaction [86], organic chemistry [87] and many others.

A similar study that employed three different visual representations confirmed the positive impact of the model in improving students' understanding of electrochemistry as well as their motivation to learn chemistry [14]. Students were also involved in generating drawing activities in this teaching intervention. Furthermore, Stammes et al [88] emphasised that involving students in drawing chemical behaviours can benefit chemistry educators by mirroring and reflecting students' deep and actual thinking. By generating their drawing, chemistry educators have plenty of insight into students' conceptual understanding [89]. This approach could be considered for the next implementation of PcBL to emphasise that students should generate a drawing regarding chemical behaviours rather than provide a pictorial representation to be analysed.

Correlation Between Students' Understanding and Their Argumentation Skills

When the correlation between students' understanding of chemistry and the level of their argumentation skills is examined using product-moment correlation (Table 7) with a Pearson correlation coefficient = 0.062, statistically, there is a positive but very weak correlation between these two variables. This result implies that there is ***almost no linear relationship*** between students' understanding and their argumentation skills. The significance or p-value (0.723), which is much higher than 0.005, confirms that the correlation is not statistically proven. The correlation value suggests that students with a good understanding of chemistry will not necessarily have better argumentation skills, and vice versa.

The result of this study is in line with the other previous findings in an Indonesian university employing an integrated chemical literacy and socio-scientific issue (SSI) approach. Although the approach effectively improved students' argumentation skills, there was no observable correlation between students' argumentation skills and their content-related SSI mastery [90]. They found that even higher achievement students required a proper guide in order to produce a suitable claim, data, warrant, backing, and rebuttal. Considering that both studies were carried out in Indonesian universities, the similarity is understandable due to the same academic culture and experiences. The work of Ramadhani [91] in Indonesia reported the relationship between students' argumentation skills and the nature of chemical representations, but not their understanding of chemistry.

Table 8. Product-moment correlation test between students' understanding of chemistry and their argumentation skills

		Argumentation Skills	TCSU
Argumentation Skills	Pearson Correlation	1	.062
	Sig. (2-tailed)		.723
	N	35	35
TSCU	Pearson Correlation	.062	1
	Sig. (2-tailed)	.723	
	N	35	35

However, relevant research in this area revealed the opposite outcomes in this study. The different outcomes reported the positive impact of graph-oriented tasks in improving students' mastery and argumentation skills [24]. In a laboratory-based activity, students with good argumentation skills are more likely to be successful in explaining the sub-microscopic representation of chemistry concepts, leading to a better understanding [82]. Argumentation-based teaching even contributed to the improvement of students' understanding and their attitude towards chemistry [92]. All of the aforementioned studies were conducted in countries other than Indonesia, such as Taiwan and Turkey, which have cultural and societal characteristics different from those of Indonesia. Therefore, this opposite outcome is plausible. Further studies involving larger cohorts and communities are required to yield more definitive conclusions regarding this counterintuitive result.

Previous studies in the area of science and chemistry education uncovered the robust correlation between students' argumentation skills and other skills, including their understanding of the Nature of Sciences, NOS [93]**,** and critical thinking [94]**.** Other relevant studies also reported the positive impact of the context-based approach in thermochemistry and thermodynamics teachings on the students' chemical literacy [95]. In teaching socio-scientific issues, students with a better understanding gave better arguments [96]. The findings emphasise the need to explore this research area in greater depth.

4. CONCLUSION

Our findings mark the positive contribution of Pictorial-based Learning (PcBL) in enhancing students' argumentation skills. In addition, students' scientific characters tend to be more scientifically sound on topics. Although none of the students demonstrated Level 5 argumentation skills, the positive progress in students' argumentation levels suggests consistent support for the PcBL in developing students' argumentation skills. The missing Level 5 may also critique how to effectively implement this approach in subsequent chemistry teachings. While this study revealed a positive effect on chemistry concepts acquisition, the correlation between students' understanding of chemistry and their argumentation skills level is delicately weak. This study provides a strong foundation for exploring the use of PcBL to enhance the quality of chemistry teaching. Reflecting on the previous works [14], [88], developing this PcBL for students to generate a pictorial representation may be reasonable.

Implications for the study

Utilising visual aids to promote students' argumentation skills [97], which incorporate a strong understanding of chemistry, is relevant to the Multimedia Learning theory and cognitive load theory [43], [47], [48]. The pictorial representations elicit students' higher-order thinking, including argumentation skills, while the amount of information stored in students' short- and long-term memories is reasonable. Although the impact of the PcBL on students' argumentation skills and their understanding of chemistry over the four topics (SIF, GL, KMT, and Thc) is noticeable, a cautious approach to applying this method in future chemistry teaching and research is recommended. While the pictorial trigger stimulated students' cognitive processing, resulting in deeper engagement with chemistry learning, other variables—including the nature of the chemistry concepts, students' spatial ability, prior knowledge, and other potential factors that could influence the intervention outcome—should also be taken into account. The subsequent study should explore the most effective strategy to enhance the effectiveness of pictorial triggers by utilising advanced technologies, including Virtual Reality (VR), Artificial Intelligence (AI) features, and other 3D technologies, to assist students in extracting necessary information and transforming it into effective chemical behaviours.

Limitations of the study

The single-group design, regarded as a weak experimental design, may limit the transferability of this study's findings. Therefore, future research involving a larger population and utilizing a stronger experimental design, such as a two-factorial or Solomon four-group design, is recommended. Moreover, the diverse nature of the topics and various types of questions may have also influenced the outcomes. In addition, due to the limited time, students' argumentative answers on each topic were not returned. Therefore, it may be beneficial to mark, return students' answers, and discuss them to provide feedback, thereby optimally building their argumentation skills.

AI-assisted technology statement

In the preparation of this work, the writers utilised Grammarly to improve linguistic clarity and to detect and rectify certain misspellings. Following the use of this tool, the authors meticulously evaluated and revised the information as necessary, assuming full responsibility for the publication's content.

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Research Article

Occurrence, Abundance, and Distribution of Microplastics in the basins of Kabani River, Wayanad, Western Ghats, India: A Baseline Assessment

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Abstract. The large-scale production of plastics and their subsequent dispersal into water bodies have harmful impacts on aquatic environments. Despite being major manufacturers of plastic waste, developing countries have inadequate research on microplastics in freshwater ecosystems. This study examines the occurrence, abundance, and distribution of microplastic particles in the basins of the Kabani River, a region of the Western Ghats in Wayanad. The sampling was conducted at eight study stations across the Kabani River basin and analysed for microplastics using a density separation method. Identification of the microplastic particles was made using Fourier Transform Infrared spectroscopy (FTIR) with Attenuated Total Reflectance (ATR). The average abundance of microplastics collected from the major tributaries of the Kabani River was 0.103 ± 0.18 particles/L (median 0.0135 particles/L) during the study. Ethylene Vinyl Acetate (EVA) was the prevalent polymer collected in the samples. As Wayanad's first report on microplastic particles in the Kabani River, this study catalyzes additional investigation into the distribution and effects of this new contaminant on the biota of several aquatic systems throughout Kerala and India.

Keywords: Kabani, Microplastics, River, Wayanad, Western Ghats

1. INTRODUCTION

Plastics are a subset of polymers, first produced in large quantities in the 1950s[1], playing a crucial role in present-day society worldwide[2, 3]. The application of plastics in recent years has increased rapidly, from domestic units to industry, owing to their low production cost, resistance, durability, flexibility, and wide range of uses[4]. The synthetic polymers such as high density polyethylene (HDPE), low density polyethylene (LDPE), nylons, poly-propylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polybutylene terephthalate (PBT), polystyrene (PS) and polyurethane (PUR) are get fragmented due to mechanical treatments and photochemical transformations triggering the development of microplastics (< 5 mm) or nanoplastics (< 1 µm)[5, 6].

Current lifestyles have necessitated the excessive use of plastics. It's delayed biological decomposition and increased persistence improves people's lives, but if not disposed properly, they accumulate in the environment and cause long-term ecological imbalances[7]. Freshwater systems act as reservoirs where microplastics can accumulate, affecting aquatic organisms through ingestion, entanglement, and habitat disruption[8]. Freshwater habitats have generally received less scientific scrutiny than marine systems regarding microplastic pollution[9, 10]. However, recent research has highlighted the fact that freshwater systems, most notably rivers, act as critical pathways for transporting microplastics from onshore sources into the ocean[11].

Rivers and streams are the source of nearly two-thirds of the world's drinking water and are becoming polluted by microplastics[12]. The ingestion of microplastics by aquatic animals increases both chemical and physical risks, potentially leading to adverse health effects[13]. Microplastics can act as carriers for toxic compounds, facilitating the transport of hazardous substances through the aquatic food web, which in turn promotes bioaccumulation and biomagnification[14]. Additionally, microplastics can act as potential surfaces for microbial colonisation, further strengthening ecological and health risks[15].

Wayanad district, a part of the Western Ghats, is situated on the southern tip of the Deccan plateau and is drained by the Kabani River and its tributaries[16]. The Kabani River is a vital water source for both ecological and human needs. The study report by the Kerala State Council for Science (2009), Technology and Environment and the Centre for Water Resources Development and Management[17] indicated that the Kabani River was the least polluted in Kerala, a finding subsequently corroborated by the Pollution Control Board of Karnataka and the Central Pollution Control Board (2017)[18]. However, later in 2021, according to studies by the Karnataka State Pollution Control Board, the river was found to be polluted due to the relentless discharge of sewage, industrial waste, and other effluents, rendering it unfit for drinking[19]. Conservation concerns, including pollution, deforestation, and unregulated human practices, pose threats to the Kabani River's water quality, aquatic biodiversity, and overall ecosystem health. Recent observations have revealed that the illegal dumping of solid waste, combined with algal blooms in many parts of the Kabani River, poses a serious threat to the aquatic ecosystem of the water body[20]. The drastic change from the least polluted to the most polluted condition of the Kabani River basin is a serious concern to the researchers.

Identifying and quantifying microplastics in river systems is essential for understanding their sources, transport dynamics, and fate within freshwater environments[21]. Among the several anthropogenic stresses on aquatic ecosystems, the accumulation of plastic trash is one of the most conspicuous yet least studied. Microplastic research is still in its early stages, and there is a significant lack of data on the occurrence, abundance, and distribution of microplastics in freshwater riverine ecosystems[22]. The current study designed to examine the distribution pattern of microplastics in Kabani River to monitor the condition and health status of the river basins. Since Kabani River is the primary water source for people and animals in the Wayanad district, a thorough assessment of microplastic contamination in the river is crucial for improving and developing plastic cycle models and for formulating efficient mitigation strategies.

MATERIALS AND METHODS

1.1. Study area

Wayanad district of the Western Ghats (latitude 11^0 27' and 15^0 47' North and 70^0 27' East longitude), is a hill station, covers an area of 2130 sq. km with an altitude that varies from 700 to 2100 m above mean sea level. It is located in the North-Eastern region of Kerala, India[23]. The Kabani River is one of the significant water bodies in Wayanad and one of the eastward-flowing rivers in Kerala, with a total basin area of 7,060.362 km^2 that spans across the southern Indian states of Kerala, Karnataka, and Tamil Nadu[24]. The study concentrated on eight sampling stations along the Kabani River basin (Table 1, Fig. 1), each station was strategically selected based on a variety of ecological and environmental conditions to ensure systematic coverage of microplastic polluted areas.

Table 1 Study stations

Stations	Location Description	Latitude	Longitude
Koodalkadavu (KO)	Anthropogenic activities such as washing, bathing, and providing drinking water for domestic animals take place, Agricultural area	11.7986	76.0747
Panamaram (PA)	Near KWA Pump House, used for irrigation, agricultural land nearby	11.8018	76.0142
Mananthavady (MN)	Near KWA pump house	11.8029	76.0039
Thirunnelli (TH)	Temple-pilgrimage activities	11.9081	75.9971
Begoor Bridge (BE)	Near forest area	11.8476	76.0853
Kuruva Island (KU)	Tourist area, forest area, effluent discharge from outside sources. Urban runoff sink	11.8283	76.0897
Valliyurkavu (VA)	Temple accompanied by Oottupura and a marriage hall nearby	11.8040	76.0290
Choottakadavu (CH)	Downstream of Mananthavady Puzha, Housing board	11.8014	75.9910

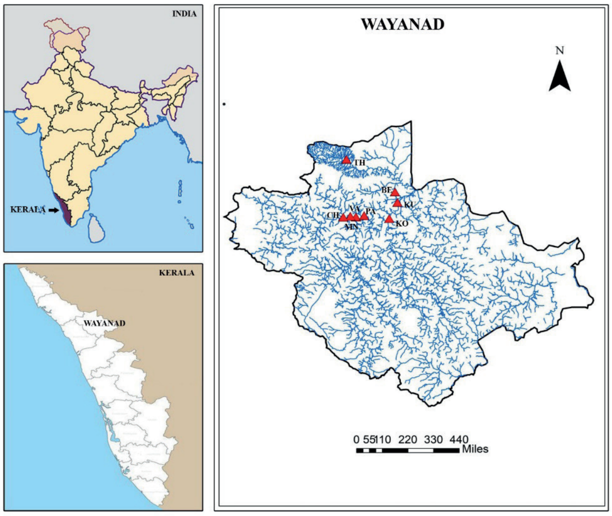

Fig. 1 Sampling stations in Kabani River basins

1.2. Sampling

The samples were collected from each study station between the tail end of winter and the onset of summer 2024, during which period the amount of rainfall was largely deficient in Kerala state[25]. Sampling was conducted in the stations Thirunnelli and Begoor Bridge during the late winter period (last week of January), and the remaining stations were covered during the last week of February and the first week of March (summer period). Plankton net with a mesh size of 60 micrometres, having a mouth area of 0.126 m^2, used for sampling. River flow velocity was determined using the float method[26, 27]. Samples were collected by anchoring the plankton net in the middle of the river channel, with the net mouth positioned half dipped (effective mouth area = $0.063m^2$) for a duration of 5 minutes. The average river flow during the sampling period was 0.053±0.025 m/s. The volume of water filtered was calculated based on the effective mouth area and river flow velocity.

1.3 Sample analysis

Collected samples are passed through the different mesh size sieves or filters to separate microplastics by size. To prevent contamination, all parts of the net were thoroughly rinsed with fresh water before use. The collected samples were transferred into a beaker containing a significant amount of organic matter that needs to be separated from microplastics. Thoroughly rinse the container with a wash bottle to make sure that all of its contents are collected. Organic contents in the collected samples were digested by using 10% of potassium hydroxide (KOH) solution. To avoid contamination, cover the beaker with aluminium foil and kept it for 24 hours to complete digestion process. The aliquots of the sample were placed in petri dishes for further analysis after digestion. The identified microplastics were classified according to their size, colour, and morphotypes (line/fibre, fragment, foam, or film), following the criteria defined by Free et al[28]. Microplastics were carefully collected and transferred into glass containers using stainless steel needles and laboratory forceps.

At most care was taken during each step of the sample collection and analysis to prevent any external contaminations. The entire field and laboratory work was carried out according to the contamination protocol[29, 30, 31]. Aluminium foils and steel containers were used throughout the sample collection and storage and whenever not in use the samples were covered with aluminium foil. To avoid particulate pollutants, all chemical solutions and distilled water were filtered through 0.45um pore-size filter paper. All the activities and analysis, including sample collection, processing and microplastic isolation, were performed wearing cotton lab coats and nitrile gloves to avoid airborne contamination and synthetic fibre from clothing. The working area and stereo zoom microscope were cleaned before any analysis using alcohol. Field and laboratory blanks were included during the collection time and microplastic isolation in the laboratory. Both blanks showed negative results.

The chemical composition of isolated microplastics was analyzed using PERKIN ELMER Spectrum 100 Fourier Transform INFRARED spectroscopy (FTIR) with Attenuated Total Reflectance (ATR). All samples of enough size were exposed to 30 scans, using a resolution of 4 cm^{-1} within a wavelength range of 4000–650 cm^{-1}. Polymer identification was carried out by comparing the obtained spectra with those in the spectral database of common synthetic polymers, previously published data, and open-access databases.

Standard Deviation, Median and range, were used to describe spatial patterns in microplastic concentration. Formal Hypothesis testing (eg. Kruskal – Wallis) was not performed due to the absence of replicate samples per station. Stations classified as Rural/Urban (KO, PA, MA, VA, CH: near settlements/bridges) vs Forest (KU, BE, TH: forested catchment reaches) based on field observations and land-use characteristics.

Microplastic impacts are evaluated using the Coefficient of Microplastic Impact (CMPI). The CMPI evaluates the impact of microplastic shapes and is calculated using the formula: CMPI = (Number of a specific microplastic shape)/(Total number of microplastics) Based on the CMPI value, impact levels are classified as follows:

- 0.0001–0.1 (minimum)
- 0.11–0.5 (average)
- 0.51–0.8 (maximum)
- 0.81–1 (extreme).

2. RESULTS

2.1. Abundance of Microplastics

Microplastics obtained from the Kabani River ecosystems were categorized according to size, colour, and morphotype. The size of microplastics found in the riverine samples varied from 0.06 mm to 5 mm, with the most abundant sizes found in the range of 0.063 mm to 0.25 mm. A 63 μm sieve was used during filtration to capture particles within this microplastic size range. Fibres were the most predominant morphotype of all recognized microplastics. The majority of the microplastics were filamentous and long, existing in bundles, with the prevalence of fibres among the observed microplastic morphotypes stemming from their multiple origins and physical characteristics. A total of 237 microplastics recorded during the study period, all of which were filamentous fibres, giving a CMPI vale of one. This corresponds to an extreme dominance of fibres over other morphotypes.

Table 2. Descriptive statistics of microplastic concentration across eight stations (n=8). Values derived from single plankton net tows. (1000 L filtered /station).

Statistics	**Values (Particles/L)**
Mean	0.103
Sample SD	0.18
Median	0.0135
Minimum	0.002
Maximum	0.47
Urban median (n=5)	0.19
Forest median (n=3)	0.002

The presence of microplastics was recorded at all study stations, although concentrations varied. The mean concentration of microplastics gathered from the principal tributaries of the Kabani River was 0.103 ± 0.18 particles/L (median 0.0135; range 0.002-0.47). (Table 2) The highest concentration occurred at KO (0.47 particles/L), the Koodalkadavu confluence where PA (0.3 particles/L) and MA (0.019 particles/L) rivers merge, combining their microplastic loads (Figure 2). Among forest stations, KU Island showed elevated values (0.02 particles/L) compared to TH/BE (0.002 particles/L), reflecting downstream transport from the KO confluence. This created a clear longitudinal gradient: confluence peak → depositional island → low headwater forest. The population, geographical terrain, hydrological factors, and river velocity are the significant environmental and anthropogenic drivers of microplastic distribution in these areas. Rural/urban-proximate stations showed substantially higher median concentrations (0.19 particles/L) than forest sites (0.002 particles/L), a ~95-fold difference driven by KO (0.47 particles/L) and PA (0.3 particles/L) (Table 2). This pattern aligns with land-use pollution gradients reported across Indian rivers[32, 33, 34].

Four prominent colours of microplastics found in our study: red, blue, green, and transparent. Red-coloured microplastics were commonly seen, while blue, green, and transparent microplastics were less common. Red fibres were dominant, particularly at Kuruva Island (57%) and Panamaram (47%). Green fibres were most common at Valliyurkavu (44%), reflecting a site-specific difference. Other colours, such as blue and transparent, occurred in lower and more variable percentages at all stations (Fig. 3). This reflects spatial differences in microplastic sources and inputs within the Kabani river system.

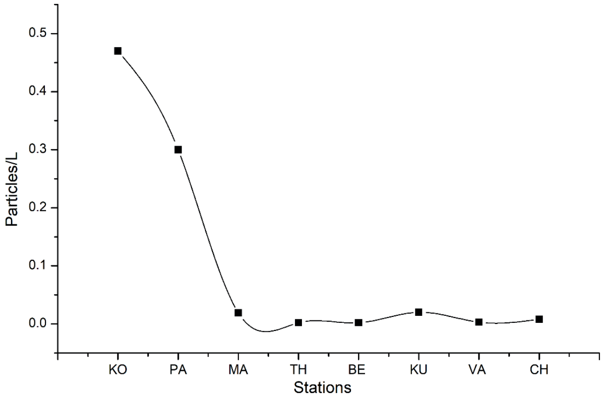

Fig. 2. Abundance of microplastics in different stations

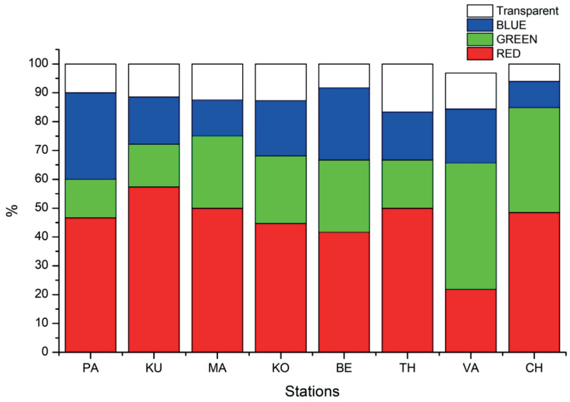

Fig. 3 Percentage composition of microplastics based on colour

2.2. Polymer identification using FTIR

Fourier Transform Infrared Spectroscopy (FT-IR) was carried out to determine the polymer composition of the collected microplastics. The FT-IR analysis indicated that Ethylene Vinyl Acetate (EVA) was the prevalent polymer in the samples. The FT-IR spectra, as shown in Fig. 4, confirm the occurrence of characteristic absorption bands for EVA, such as peaks of C–H stretching, C=O stretching, and C–O bending vibrations.

The identification of EVA in the collected microplastic samples suggests that industrial products, such as footwear and packaging materials, may be potential sources of microplastic pollution in the study area. Microscopic examination (Fig. 5) revealed the association of microplastics with algal material, providing insight into the potential interaction between synthetic particles and aquatic biota (Fig. 5d).

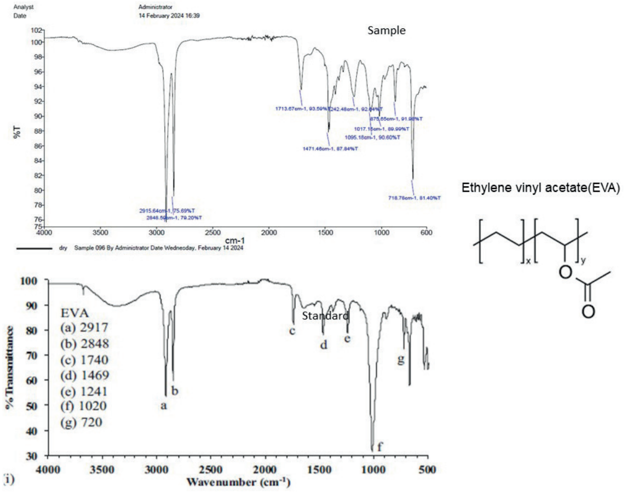

Fig. 4 FT-IR spectra analysis of microfibres with standards.

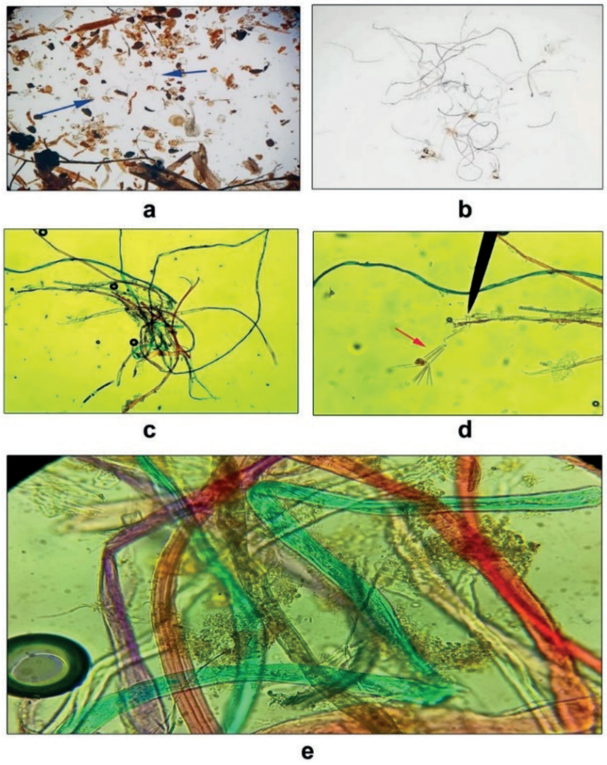

Fig. 5 Microscopic image of microplastics

a. a – Assorted microplastics (0.75x magnification) from the sample
b. b, c, d (arrow mark indicated algal association) and e - Sorted microplastic particles (2x, 4x and 100x magnification).

Discussion

Urbanization and anthropogenic activities have introduced numerous harmful substances into the ecosystems, particularly plastics[35]. India is one of the leading plastic consumers globally, utilizing plastics in day-to-day human life as the most flexible artificial product[36]. Microplastics were first identified in 2004[37] and are now documented as prevalent contaminants in both aquatic and terrestrial ecosystems[38, 39].

Fibres were the principal morphotype of microplastics recorded in our study among the 237 microplastics. Many scientific studies recorded similar observations in which fibres to be the most abundant type of microplastics, particularly in water bodies, sediments, and organisms. Higher fibre dominance (>90%) were recorded on beach sediments of USA with ~93% of microplastics being fibres, well above fragments and other forms[40]. McNeish et al.[41] studied on fish samples and riverine water from the Gulf of Maine, microfibres accounted for 97-100% of microplastics. Densely populated areas such as Koodalkadavu, Kuruva Island, and Panamaram have shown a high concentration of fibres in our study. Effluents from laundering synthetic textiles, improper waste management, agricultural runoff, and fishing gear and sanitization products have contributed the high fibre load in these regions. A study report of Anagha et al.[42] in the Vembanad Lake, one of the Ramsar sites in Kerala, fibres dominated over 50% of entire microplastics collected in subsurface and bottom waters with polyamide and polypropylene polymers, which are suspected to have been released through fishing and laundry wastewater, further supporting the abundance of fibres in the aquatic system.

Begum et al.[43] reported that 79.4% of microplastics in water samples and 89.8% in sediment samples were constituted by fibres in the Palar River Estuary, Southeast Coast of India. Similarly, an investigation into the Periyar River revealed that fibres were the predominant form of microplastics, with a higher concentration observed during the monsoon season[44]. These results suggest that the fibres and fragments were the most prevalent morphotypes recorded in both northern and southern India[45]. The exclusive presence of fibres suggests substantial influence from textile, fishing lines or ropes and other fibrous materials transported via domestic wastewater and surface runoff, a pattern commonly reported in riverine microplastic studies[46, 47].

The mean concentration of microplastics obtained from the major tributaries of the Kabani River was 0.103 ± 0.18 particles/L (median 0.0135; range 0.002-0.47) which is relatively lower compared to the other major rivers in Kerala. A related microplastic abundance of 15.13 ± 4.13 – 170 ± 17.75 particles/L were observed from the eight sampling stations along the Chalakudy River of Kerala by Kumar et al[48]. These differences might be owing to changes in population density and minimal industrial activity in the Kabani River basin. The 95-fold urban-forest gradient (0.002–0.19 particles/L medians) reflects direct settlement inputs at KO/PA versus dilution/transport at forested reaches. KU (0.02 particles/L) shows intermediate pollution from upstream PA/MA runoff accumulation, consistent with riverine microplastic transport dynamics. Kabani maintains low overall abundance compared to urban Indian rivers (0.3–4 particles/L).

A comparatively low microplastic abundance recorded in the Kabani River with other urban Indian rivers can be attributed to reduced human pressure within riverine basin. Major urban rivers in South India including Adyar, Cooum, and Kosasthalaiyar rivers, for instance, have already been known for the presence of significant amount of microplastic discharged from domestic sewage and effluents from industries[49, 50, 51]. However, Kabani River drains mainly from rural and forested Western Ghats is under lesser population density and fewer industries, thereby restraining constant microplastic inputs[52]. Similar studies have also been recorded in riverine basins of South India, where lower microplastic densities noted in rural river systems emphasizing that land-use characteristics, along with population density, affect microplastic levels[53].

The pronounced microplastic gradient reflects river confluences and depositional geomorphology characteristic of Kabani River. Koodalkadavu (KO: 0.47 particles/L) represents a confluence hotspot where PA and MA tributaries deliver cumulative urban runoff from settlements and bridges, consistent with tributary merging as microplastic concentration maxima in river networks. Downstream Kuruva Island (KU: 0.02 particles/L) functions as a secondary depositional sink, where low-velocity eddy systems trap fibres transported from KO during summer baseflow conditions (0.053±0.025 m/s). Headwater forest stations TH/BE maintain baseline levels (0.002 particles/L) distant from settlement influences. The spatial distribution pattern of microplastics along the study stations highlights a strong longitudinal and land use related aspects with the highest concentration at the KO confluence and a progressive decrease towards the forested areas. This higher microplastic concentration at KO can be recognized by the hydrological merging of PA and MA rivers, that outcomes convergence point getting total input sources from the upstream areas, agricultural effluents and waste water discharge. The confluences are known areas for microplastic accumulation and thereby noticing decrease in the velocity of the flowing waters, increased sedimentation rates and the highest pollutant load in the tributaries[54].

The observed association between algae and microplastics strongly indicate the biofilm formation, which is likely to alter microplastic resistance, degradation, and increase the ingestion rate by aquatic animals[55]. This association may facilitate trophic transfer and warrants a more thorough ecological risk assessment.

The red, blue, green, and transparent colours of microplastics obtained in our study, in which red coloured fibres were commonly observed, and transparent fibres were less common. Meanwhile, seven colours, including brown, red, orange, green, blue, violet, and grey, have been separated from the Pasig River in the Philippines[56] and eight different colour groups of plastics were examined in the Chalakudy River[48]. Coloured microplastics can be easily ingested by aquatic invertebrates and vertebrates, which may negatively impact trophic interactions and ecosystem functioning[57, 58]. Singh et al.[59] examined the occurrence and dynamics of microplastics in the Ganga River basins surrounding the city of Varanasi, recorded different sources and compositions of microplastics with the predominant colours found to be blue, brown, white, and some other shades, displaying site-specific patterns. In a similar work relating microplastic contamination of Mandovi-Zuari system of Goa, an estuarine environment situated on the west coast of India, Gupta et al.[60] found that the blue and green-tinted microplastics were predominant in surface and sediment water samples. The presence of coloured microplastics within the freshwater environments indicates the continued exposure of water sources and anthropogenic activities.

The detection of ethylene–vinyl acetate (EVA) among the recovered microplastic polymers suggests inputs from industrial products, mainly parts of footwear, sports goods and packaging foams. EVA has been broadly accepted and used in industries owing to its light, flexible, and shock-absorbing nature, and its natural occurrence has gradually been integrated into the abrasion and fragmentation of footwear, mats, and packing wastes in urban and natural environments[61]. In riverine environments, EVA particles can be introduced either through the surface runoff, inadequate dumping of solid waste, or from the market places with frequent human activities. Despite the absence of huge industrial infrastructure in the Kabani River basin, the presence of EVA indicates it's diffused, non-point sources related to human activities. Such observations were likewise found in other Indian and worldwide freshwater resources, wherein EVA and other copolymers were traced to footwear deterioration, recreational use, and semi-urban community discharges[50, 51].

3. CONCLUSION

This research is the first investigation to undertake a comprehensive assessment of microplastic contamination in the Kabani River, which is an important freshwater ecosystem in the Western Ghats region of Wayanad district, Kerala. The confirmation of the microplastic across all the study stations reveals the prevalent nature with an average abundance of 0.103 ± 0.18 particles/L. Remarkably, higher concentrations of microplastics were recorded in overpopulated and tourist-frequented areas such as Kuruva Island, Koodalkadavu, and Panamaram, suggesting that anthropogenic influence is a key contributor. The fibres emerged as the major microplastic morphotype and coloured (red, blue, and green) and transparent particles were significantly prevalent. The FT-IR spectroscopy (PERKIN ELMER Spectrum 100) identified Ethylene Vinyl Acetate (EVA) as the predominant polymer in the study stations, pointing to its widespread usage and environmental persistence. These findings emphasize the immediate need for more stringent regulatory measures, public awareness campaigns, and source-specific waste management practices to mitigate microplastic pollution in ecologically sensitive riverine ecosystems. To protect, biodiversity and water quality of Kabani River, future research should emphasize on long-term monitoring, source identification and ecological and environmental impact assessments.

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Research Article

The Suppression of the Cambridge University Department of Colloid Science

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Abstract. The Cambridge University Department of Colloid Science, founded in 1930, was suppressed by the University after the retirement of the Department Head, Roughton, in 1966. The closure was long and acrimonious, requiring two debates in the University Senate House and a University-wide vote. Decisions were taken by committees that included three Nobel Prize winners and many distinguished Cambridge scientists, but there was little consultation with the wider UK colloid science community, either academic or industrial. In times of financial stringency it is sometimes necessary to close university departments, and this review of an unsatisfactory closure may help future generations of university administrators to avoid some of the potential pitfalls.

Keywords: Colloid Science; Department Closure, Cambridge

1. INTRODUCTION

The suppression of the Cambridge University Department of Colloid Science (CUDCS), proposed by the University authorities on the retirement of the Department Head in 1966, was sufficiently controversial that it was debated in the University Senate House. I found the debate[1] in the *Cambridge University Reporter* during my time as a research student in the 1970s, but only now have I been able to investigate this affair, which is mentioned explicitly in the memoirs of Mott.[2]

My curiosity was further raised when I saw that the University Library contained relevant papers, with a catalogue entry stating "Some items are restricted at the discretion of the Keeper of Manuscripts".[3] All the actors in this affair are now dead, and as far as I am aware my access to the papers has been unrestricted.

Colloid Science, including both colloid physics and colloid chemistry, is an interdisciplinary subject lying on the boundaries of several traditional disciplines, including biophysics. Overviews of the areas included in the field are in the two-volume texts by Alexander & Johnson[4] (both sometime members of the CUDCS) and by Kruyt & members of the strong Dutch colloid community.[5] Journal titles indicate the extent of the field: Journal of Colloid and Interface Science, Colloid and Polymer Science, Soft Matter, Colloids and Surfaces A: Physicochemical and Engineering aspects, Colloids and Surfaces B: Biointerfaces.

It is difficult to encourage interdisciplinary collaborations within a university, where teaching (and therefore research) tends to be organized along the lines of traditional disciplines. Exceptions include chemical engineers, who require skills in both chemistry and engineering, and applied mathematicians, who are happy to use mathematics to solve problems in any field. Here we look at the history of a university department formed with the express aim of fostering interdisciplinary research: the Cambridge University Department of Colloid Science, which studied areas of interest both to Physical Chemistry and to the emerging field of Biophysics, a field which had come to prominence with the publication[6] in 1953 of the double helix structure for DNA by Watson & Crick, working in Cambridge.

2. EARLY HISTORY OF THE DEPARTMENT

In 1928 the Rockefeller Benefaction for the new Cambridge University (C.U.) Library and for Agriculture, Biology and Physics was announced,[7] from which the chair of colloidal physics was created in 1930, with E.K. Rideal[8] as the first Professor. Soon afterwards, the John Humphrey Plummer bequest to the University provided funds for new chairs. The chair in colloidal physics was allowed to lapse, and Rideal was appointed to a Plummer chair. Such chairs came without any departmental administrative duties, allowing Rideal to concentrate on research. The appointment of Rideal led to a division between his group and that of T.M. Lowry,[9] the Professor of Physical Chemistry, recounted by Tabor.[10]

In 1943 it was proposed to re-organise[11] the Department of Chemistry to form a Department of Colloid Science and a Department of Chemistry (with sub-departments of Inorganic, Organic, Physical and Theoretical Chemistry, and of Metallurgy). Rideal had requested that "since Colloid Science includes the Physics and Chemistry of Colloids and their application to Biology, his laboratory should be in a position to collaborate with the biological Departments and should not be an integral part of the Department of Chemistry." But by January 1944, prior to the arrival of A.R. Todd[12,13] as Professor of Organic Chemistry, this proposal was changed[14] to a division into Departments of Colloid Science, Metallurgy, Physical Chemistry, and Organic & Inorganic Chemistry. Thus, quite apart from Colloid Science, Chemistry itself was divided into two separate departments, headed by Todd (Organic) and Norrish (Physical). "Their personal relationship was cool"[15] and the two departments were combined only in 1986.

In 1946 Rideal resigned in order to go to the Royal Institution as Professor of Chemistry and director of the laboratories.[16] He took with him his research student Paley Johnson, who subsequently returned to take up a CUDCS lectureship in 1950.

The following year Dr F.J.W. Roughton[17] (C.U. lecturer in Physico-chemical aspects of physiology) was elected to replace Rideal.

The history[16] of the Department up to 1962 is recorded and discussed by D.A. Haydon[19] & R.H. Ottewill[20] who in 1962 were Assistant Directors of Research (ADR, an untenured position, typically held for five years) in the CUDCS. Haydon & Ottewill were helped by a series of Annual Reports[21] which listed the staff of the Department, their current teaching and research activities, and their publications.

In a Senate House discussion[1] concerning the closure of the CUDCS (to be discussed in Section 3), Roughton states that Haydon & Ottewill's history was in response to an invitation from the Society of Chemical Industry. The nature of this weekly journal was such that it would have been easy for Roughton to suggest to the editor that there was scope for such an article.

Figure 1 shows a 1961 group photograph of members of the CUDCS, including, on the front row, Haydon, Johnson, Roughton and Ottewill. There is no need to repeat the content of Haydon & Ottewill.[16] However, two items caught my eye and merit comment.

2.1 The Oppenheimer Laboratory

J.H. Schulman was appointed ADR[16] in 1937, and eventually promoted to a personal readership.[21] In 1949 the Rhokana Corporation donated funds that were used to set up a laboratory in Cambridge, on the Madingley Road, to study surface chemistry, especially effects that play a role in the flotation process used in the mining industry.[16] The work was directed by Schulman, and was sufficiently successful that in 1952 the Rhokana Corporation donated additional funds (£146,650) for the permanent endowment of work in Surface Chemistry, to be known as the Ernest Oppenheimer Fund. As long as Schulman continued as Reader in surface chemistry, the fund was to be used to support research under his direction, in particular, research on the application of surface chemistry to metallurgical problems.[22]

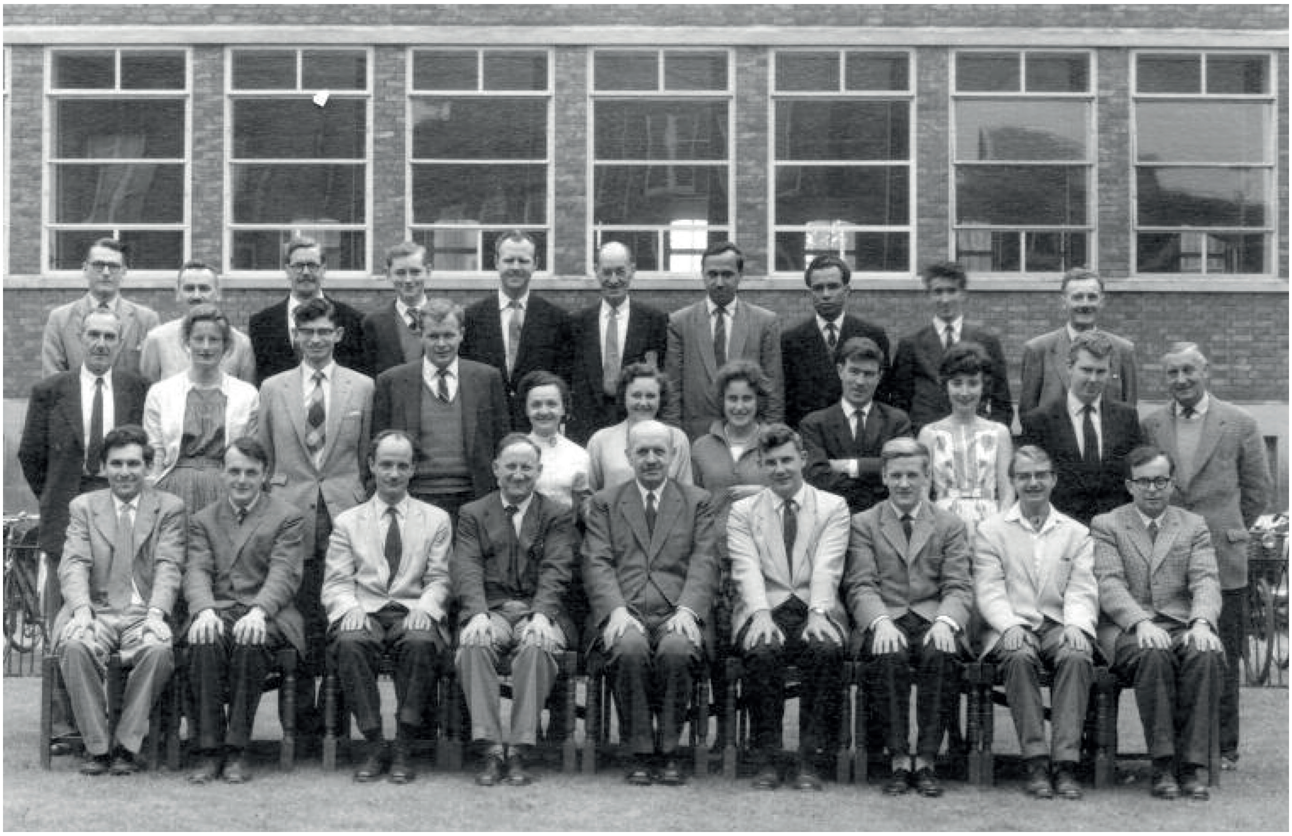

Figure 1. Group photograph of the Colloid Science Department in 1961. On the front row, positions 3–6 (from the left), are Haydon, Johnson, Roughton and Ottewill. © University of Cambridge.

Schulman resigned in 1957 on being appointed Professor of Chemical Metallurgy at Columbia University. As a result, the Oppenheimer fund became available for work other than that directed by Schulman, and the regulations concerning the fund were changed to reflect this.[23] The Report of the Council[24] and subsequent Senate House discussion[1] indicate that there was a general acceptance that the fund was intended by its donors to be used for inorganic surface science. Current practice is that the fund (the capital of which had risen by July 2024 to over £10 million[25]) is used to finance the Ernest Oppenheimer early career Fellowship.

In the Senate House discussion,[1] Roughton stated that one of the chief reasons for Schulman's resignation was uncertainty surrounding what would happen to the Department on Roughton's retirement in September 1966. Schulman could not expect to be promised Roughton's chair in advance, and it is only normal that when offered a chair in the USA he decided that a bird in the hand was worth two in the bush. This was a period when pay and conditions in the USA were sufficiently attractive that many scientists left the UK, a phenomenon known as the "Brain Drain".[26]

The precise location of the Oppenheimer Laboratory at High Cross is not stated by Haydon & Ottewill:[16] it can be found on Ordnance Survey maps published in 1970 and 1972, labelled "laboratory" and recognizable due to its footprint.

The laboratory eventually became a store for the Museum of Archaeology and Anthropology, and was vacated during the academic year 1984–85 to allow the site to be redeveloped for the British Antarctic Survey.[27]

2.2 Weissenberg

A rheological group was established within the Oppenheimer laboratory, directed by Dr K. Weissenberg,[28] after whom is named (i) an effect, (ii) a Dimensionless Number, and (iii) a scientific instrument. The Weissenberg effect is the tendency of some elastic (e.g. polymeric) liquids to climb up a vertical rotating rod inserted into the liquid free surface (perhaps in order to mix the liquid). The Weissenberg number is the ratio of elastic forces to viscous forces in a flowing elastic fluid. The Weissenberg rheogoniometer[29,30] was a versatile device for measuring all manner of rheological flow properties of liquids, though this versatility made the device complicated and not the first choice for simple measurements (e.g. viscosity). Little has been written about Weissenberg's links to Cambridge: his papers are now in the archives of Churchill College (not founded until 1960). Despite Weissenberg's international reputation, he seems not to have held a C.U. post, but acted as a consultant to the Ministry of Supply 1950–58, based in Cambridge. He supervised Grossman's thesis,[31] a copy of which was issued as a report[32] of the Armament Research and Development Establishment, Langhurst, Sussex. Weissenberg is mentioned in the CUDCS annual reports[21] for 1955–56, 56–57 and 57–58.

3. ROUGHTON'S RETIREMENT

After Schulman's resignation in 1957, Roughton wished to sort out the future of the Department, of the readership vacated by Schulman, and of the Oppenheimer Fund. He consulted the Faculty Board of Physics and Chemistry,[1] who referred the matter to the General Board of the University. It became clear that decisions concerning the future of the Department could not be made before decisions concerning the Plummer Professorship of Colloid Science, which would become vacant on Roughton's retirement.

It was therefore decided in 1959 to establish a Plummer Professorship committee to discuss these matters.[33] The committee was chaired by the Vice-Chancellor, Prof. Sir Herbert Butterfield (a historian), with members Prof. Sir William Hodge (Pure Mathematics), Prof. Sir Nevill Mott (Physics), Dr H. Godwin (Botany), Prof. R.Y. Jennings (International Law), Prof. Sir Alexander Todd (Organic Chemistry), Prof. R.G.W. Norrish (Physical Chemistry), Prof. F.G. Young (Biochemistry), and Prof. Sir Bryan Matthews (Physiology). The committee interviewed Roughton, and considered written documents including the annual Departmental Reports and other documents prepared by Roughton concerning the history and future work of the Department. However, it took no evidence from other members of the CUDCS, and the Faculty Boards were not consulted.[1] It concluded, in a report[24] dated 18 July 1960, that (a) on Roughton's retirement, his Plummer chair should become a chair of Biophysics, (b) the CUDCS should be wound up, and provision made for the creation of a Department of Biophysics, and (c) that if recommendations (a) and (b) were accepted, consideration should be given (i) as to which of the current work of the Colloid Science Department should be continued (and where), and (ii) to the use of the income of the Oppenheimer fund.

Roughton states[1] that he was shown this report, in confidence. The University did not wish to impose a ready-made team on a new Professor of Biophysics,[34] though it recognised that Haydon's work would be relevant and was prepared to offer him a 5-year extension of his ADR up to 31 December 1968. Ottewill, however, would only be offered an extension from 31 December 1963 to 30 September 1966 (Roughton's retirement). Johnson, a lecturer with tenure, would perhaps be moved to Biochemistry. Roughton fought for Ottewill to have parity with Haydon,[35] but to no avail. This difference in treatment was not something that anyone wished to announce to those concerned.[36]

However, in January 1963 Ottewill was offered a post at Bristol by the Head of the Department of Physical Chemistry, Professor D.H. Everett,[37] and sought advice from Roughton concerning the future of the CUDCS. Roughton sought (and was granted) permission from the General Board to inform his staff of some of the key points in the Board's decision. Johnson states[1] "In February 1963 Professor Roughton was instructed to read out certain selected passages from these findings [the report of 18 July 1960] and from those of a subsequent sub-committee to myself and other senior members of the Department of Colloid Science. Apparently the documents were of such a confidential nature that we were not allowed to read them or even part of them for ourselves, and even now we have not seen them."

Not surprisingly, Ottewill accepted the invitation to take up a lectureship in the Department of Physical Chemistry at Bristol University, in order to establish an MSc course in surface and colloid science.[20]

In May 1965, the Council of Senate issued a report[24] concerning the Quick Professorship of Biology, the Plummer Professorship of Colloid Science, the Department of Colloid Science, the Oppenheimer fund, and the Bles Bequest (funds for Animal Embryology or more general Biology). The General Board considered the report of the Professorship committee, and agreed that the next Plummer Professorship should be in Biophysics, but decided against the immediate creation of a Department of Biophysics. They were "firmly of the opinion that the subject of Colloid Science does not warrant the continuation of a separate Department and that, subject to the University's approving the change of subject of the Professorship, the Department should be suppressed." The University Council agreed with the General Board,[24] stating that "the General Board will in due course report to the University on the suppression of the Department of Colloid Science".

However, the Ordinances of the University allow reports to be discussed in the Senate House, and such a discussion[1] took place on 25 May 1965. The first speaker, Prof. Sir Joseph Hutchinson, was concerned about the Quick Professorship and the Bles Bequest. There then followed a long, and somewhat rambling, contribution from Roughton, which takes over three and a half pages of the *Reporter*. He went into the history of the Department and its output of teaching, research publications and trained researchers destined for industry, government or academic posts. He regretted that the General Board and its committees had not sought a wider range of views concerning the future of colloid science, including those of the current members of the Department and opinion from outside the University. He felt that work on surface chemistry, colloid science and biological physical chemistry should be kept together, either as a Department or a sub-Department. He also regretted the decision not to proceed with the creation of a Department of Biophysics.

Speeches were also made by Prof. G.K. Batchelor,[38] Dr P. Johnson, Dr J.F. Davidson,[39] Dr D.A. Haydon and Prof. R.G.W. Norrish.[40] Roughton, Batchelor, Johnson and Davidson were all fellows of Trinity College, elected in 1923, 1947, 1962 and 1957, respectively. However, my own recollections of Batchelor are such that I do not believe he would allow high table friendships to take priority over what he thought right for both the University and its employees. Batchelor thought that the General Board had failed to make satisfactory arrangements for the staff of the CUDCS. Six years after Roughton first raised these issues, the Report stated only that "The General Board will in due course report to the University on the suppression of the Department of Colloid Science". Batchelor continued, "In due course? Mr Vice-Chancellor, I suggest that this is not the kind of considerate and fair treatment of the graduate and assistant staff of the Department that we expect from the University......The Report shows little appreciation of the value of an active and well-established scientific team. A good deal of capital is required to establish a research laboratory, in the form of graduate staff with complementary interests and good working relationships, suitably trained assistant staff, and a well-stocked laboratory." Batchelor, an applied mathematician, was aware of the importance of interdisciplinary science and as founder of the C.U. Department of Applied Mathematics and Theoretical Physics[38,41] in 1959 he would have known only too well the effort required to establish a scientific group. Batchelor suggested that the CUDCS should be kept together, perhaps as part of the Department of Physical Chemistry, and that a good use of the revenue from the Oppenheimer fund would be to provide a senior office in the subject of Colloid Science. "In the absence of any information about the General Board's intentions regarding the Department, other than the bald statement that it should be suppressed, I do not think it is right that the University should be asked to approve a recommendation to continue the Plummer Professorship now held by Professor Roughton in a field other than Colloid Science."

Next Johnson spoke first to re-affirm the links between biological aspects of colloid science and work on inorganic colloids; he stressed the importance to industry of a supply of trained colloid scientists. He argued that the CUDCS should be renamed (to become, presumably, the Department of Biophysics). Finally, he criticised the procedure by which decisions had been made, with the loss of an ADR (Ottewill) and of Johnson's own valuable and highly trained laboratory assistant. The uncertainty had made it extremely difficult to recruit Research Students.

Davidson (later to become head of the Chemical Engineering Department) felt that Colloid Science was important both academically and industrially, and that the subject should be encouraged rather than suppressed.

Haydon supported the idea of a Department of Biophysics, and that the Professorship of Colloid Science should be converted to one of Biophysics. "This requires no comment as the Professorship of Colloid Science has been, in everything but name, a Professorship of Biophysics for at least the last twenty years."

Finally Norrish, the outgoing Professor of Physical Chemistry and a member of the original Plummer Professorship committee, spoke. He would have liked to see the CUDCS go on as it was (perhaps with the title changed). If it had to be broken up, the Physical Chemistry Department would do anything it could to support the physical chemistry aspects of the CUDCS.

This discussion took place at the end of the Easter term 1965, just before the long vacation, and it was not until October that a Notice,[42] dated 18 October 1965 was published. As regards Colloid Science, the Board were "still of the opinion that if the University approves the change in scope of the Plummer Professor [i.e. to one of Biophysics] the Department should be discontinued... The Board, contrary to what might be supposed from some of the remarks made at the Discussion, gave very lengthy considerations to the question of the future of the staff of the Department. In reporting to the University on the discontinuance of the Department they have said that they intend, with the concurrence of the Professor of Physical Chemistry, to recommend that any officer in the Department whose tenure does not end before 1 October 1966 shall be transferred to the Department of Physical Chemistry. There remains the problem of accommodation, which the Board are reconsidering...”

It seems strange that the results of these “lengthy considerations” were not conveyed to the people concerned, and the episode seems, at best, to be a fine example of the mushroom farming approach to Personnel Management (“Keep in the dark and feed bullshit”).

The Council also agreed to submit to the Regent House (the ultimate governing body of the University, which includes all lecturers, readers and professors, together with many college fellows etc.) a separate Grace for the approval of each of the recommendations of the report.[43]

However, after the 18th October, the General Board received further representations, with a request that the recommendation concerning the Plummer Professorship should be withdrawn until more was known concerning the fate of the Department and its present staff. The appropriate Grace was withdrawn[44] on 25 October but on 8 November the Council issued a Notice[45] that the General Board considered it was “imperative to reach a decision..about the Plummer Chair without further delay.” And so the Grace was re-submitted for approval.

In 1965, if ten (or more) members of the Regent House requested a ballot, approval of a Grace was conditional on the results of such a ballot and the University Ordinances allow fly-sheets, signed by members of the university, to be published, giving reasons for (or against) the proposals. [The number of members required to request a ballot has since been increased, and in 2025 stands at twenty-five.[46]] Two such fly-sheets, dated 6 December 1965, appeared in the C.U. *Reporter*[47,48] prior to the ballot to be held on 9–10 December 1965. The first flysheet[47] applauded the proposal to create a Plummer Chair in Biophysics: such a professor would not be encumbered with the administrative burden associated with the Headship of a Department. It also supported the winding up of the CUDCS. “The term ‘Colloid Science’ is however outmoded and to-day there is, for example, little in common between research on proteins and on the dressing of ores.” The flysheet was signed by 25 members of the University, including nine of the twelve members on the General Board.

The second flysheet[48] was signed by 144 members of the University, including Batchelor, Johnson, Davidson, Haydon and Norrish, all of whom had spoken at the Senate House discussion. Many of the signatories were applied mathematicians, whom Batchelor would have found easy to canvass in the Department of Applied Mathematics. Some, such as E.R. Lapwood, had interacted with the CUDCS.[31] Even if others had little concern for Colloid Science, they would have felt solidarity with fellow University employees left in uncertainty by the University. Amongst the signatories was J.R.G. Bradfield,[49] a cell biologist and Senior Bursar of Trinity. He founded the Trinity Science Park, and probably looked favourably on the needs of industry. Joseph Needham also signed. A biochemist, he is now better remembered for his monumental work on the Science and Civilization of China. He had already formulated the “Needham Question”,[50] asking why China, which had been technologically ahead of Europe (e.g. paper, printing, gunpowder) did not develop industrially and scientifically as Europe did with its Industrial Revolution after the Renaissance. The organisation of scientific and technological research was thus of interest to him.

This second flysheet agreed that a Cambridge chair in biophysics was long overdue, but did not accept that this should be created in such a manner as to “decapitate Colloid Science”. The flysheet was glad to note that the General Board had accepted that the CUDCS should be transferred administratively to Physical Chemistry, and urged that “the graduate and assistant staff of the present Department of Colloid Science should be allowed to remain in their present premises....until suitable long-term accommodation..can be provided for them.” “The members of the Colloid Science Department as yet have no information about their laboratory working conditions in ten months’ time...they naturally feel considerable concern.”

Everyone accepted that it was appropriate that the Plummer chair of Colloid Science should become one of Biophysics. Those who argued against the Grace did so in the hope that consideration would be given to the fate of the members of the CUDCS.

In the meantime, the Chemistry Department was realising that if the two remaining senior members of the CUDCS (plus their teams) moved to Chemistry, not only would it become harder to justify additional appointments (of their own choosing) in the future, but more space would be required. They therefore requested that the CUDCS should remain in its Free School Lane laboratories. But Physics, still on the New Museums site, had its eye on these adjacent laboratories. Prof. A.B. Pippard[51] (Physics), felt he could not openly support the closure of the CUDCS lest he be accused of doing so out of self interest, so despite being on the General Board he did not sign the first flysheet. However, he sent a memo[52] to all members of the Physics Department in the Regent House (i.e. those entitled to vote) pointing out that if the CUDCS was moved to Chemistry, the Chemistry Departments would still have 770 square ft per research worker, compared to 395 square ft per researcher in Metallurgy plus Physics, and urging them "to think about the issues involved and to make a point of casting your vote."

The ballot resulted in the Grace being rejected, with 80 votes for the grace and 186 against.[53]

Mott relates the affair in his memoirs:[2] "Some departments, such as physics, were expanding because the number of students admitted by the colleges increased. So such departments applied for more staff and, funds being available, got them. But it was felt by some, particularly the Secretary-General (Harold Taylor) that even if funds were available the total number of dons should not increase. One reason was that most university teaching officers wished to be college Fellows, felt themselves second class citizens if they were not, and the places in the colleges were limited. So if there was to be expansion in—for instance — physics, there had to be compensating contraction elsewhere. But the question was—where? If a scientific department was envisaged, the professor would fight to the death for his private empire. The General Board picked on a very small department, Colloid Science, from which the professor was retiring. But even so, they could not bring it off. The department found enough friends to come and vote against the General Board tyranny. Compensating contraction seemed impossible."

This account is inaccurate in that Harold Taylor, who held the post of treasurer from 1945–53, was Secretary General from 1953 to 1961, when he was replaced by W.J. Sartain. So although Taylor was in place when the future of Colloid Science was first discussed, he had left the scene well before the discussions of 1966. Mott was himself very capable of keeping expenditure within bounds, and one of his first decisions after his appointment as head of the Cavendish (Physics) Laboratory was to cancel a project to build a linear particle accelerator in Cambridge,[54] thereby abandoning the Cavendish's leading role in nuclear physics established by Rutherford. Mott's comments concerning the desire of University teaching officers to hold a college fellowship are supported by Todd, who in his memoirs[55] states that when he went to Cambridge in 1944 "the stipend of a university lecturer was quite derisory (I think it was £150 p.a.) and included payment for a few hours of teaching.... If the lecturer was a fellow of a college he would receive in addition a college stipend plus payment for teaching or other work in college; in this way he could make quite a reasonable living. If he were not a fellow, however, he received from the university a modest 'Fellowship Allowance', but if he were to get a living wage he had to do a lot of extra teaching." So Mott's "second class citizens" suffered both poor social status and poor financial status.

Todd does not discuss the suppression of the Department in his memoirs. However, he states[56] when considering the possibility of a move to Cambridge, "There was a long history of internecine warfare between R.G.W. Norrish who was Professor of Physical Chemistry and E.K. Rideal who, although also running what was in effect a second school of physical chemistry, did so under the banner of Colloid Science." Thus for Todd, "Colloid Science" meant "Colloidal Physical Chemistry", and it would appear that even before he arrived in Cambridge he was against the existence of a separate Department of Colloid Science. Brown and Kornberg[13] report *"Both physically and as a personality Todd was a towering presence at any meeting or committee on which he served. This presence, with complete confidence in his own decision making, led to his holding a series of important positions relating to science policy and other public matters."* Whether or not Todd dominated the Professorship committee, we do not know. Mott was also on the committee, and there was at that time a saying "Todd thinks he's god; Mott knows that he's not".[57] But Todd had already won his Nobel prize in 1957, whereas Mott became a Nobel Laureate only in 1977. A third member of the committee, Norrish, was awarded the Nobel Prize in 1967, and of the three he alone supported CUDCS, signing the second (non placet) flysheet.[48] Although not a colloid chemist, he had been a research student of Rideal.[40]

In his memoirs[58] Todd reveals that when Master of Christ's College he offered the job of Senior Tutor without consulting the College Council, and as chairman of the University Press he appointed a chief executive without consulting the Syndics of the Press. Communication in the days before email and mobile telephones was harder than it is today, and time was of the essence in these appointments. Nevertheless, we can conclude that Todd was happy to keep people in the dark when it seemed necessary.

4. THE SECOND DISCUSSION

By 1968 Roughton had retired, and the CUDCS consisted only of Johnson and Haydon, with six assistant staff, and many vacancies. The possibility that members of the CUDCS should join Physical Chemistry was mentioned in the first Senate House discussion. However, in his memoirs Johnson[59] states that although Prof. J.W.

Linnett[60] (the incoming professor of Physical Chemistry on the retirement of Norrish) was initially enthusiastic, it was made clear to him "from a high university level" that any addition to his staff would mean no further appointments in the foreseeable future. So the idea was dropped.

In July 1967 the Council of the School of the Physical Sciences recommended that Johnson and Haydon's posts should be transferred to the Faculty of Physics and Chemistry.[61] Five vacant posts (one ADR, two Senior Assistantships in Research and two Assistantships in Research) would be suppressed. A temporary Committee of Management would be established to act as Head of Department, and these proposals were recommended by the General Board in a report[61] in January 1968. The 1967 Council statement also suggested that Johnson and Haydon should remain in the Free School Lane premises minus the top floor, with little-used equipment stored in the Oppenheimer Laboratory. Oppenheimer money no longer required to fund research posts could be used to improve sub-standard parts of the Free School Lane building. In a second report the Council of the Senate proposed that Roughton's Plummer chair should be continued in the subject of Biophysics.[62]

These reports were debated[63] on 20th February 1968. The only comment concerning the Plummer chair was by Roughton, who welcomed the prospect of a chair of Biophysics.

There was rather more discussion of the report on Colloid Science. Johnson pointed out that with only two senior staff (himself & Haydon) and fourteen researchers remaining, it was not surprising that laboratory space and equipment were under-used. There was a strong moral case for supporting Assistants in Research from the Oppenheimer fund, in the spirit of the terms of the original gift, rather than expenditure on buildings, and there was no case to be made for the removal of laboratory space (i.e. the top floor of the building). Johnson thought that a transfer to the Department of Chemistry, while remaining in the Free School Lane laboratories to resolve problems of space, would be a solution that removed further years of uncertainty.

Contributions by Davidson, Dr D.A. Blackadder (Chemical Engineering), and Linnett emphasized the importance of Colloid Science and urged that it should be encouraged, rather than left to decline. Haydon spoke along lines similar to those of Johnson. Roughton, though now retired, spoke at length (nearly two double-column pages in the Reporter) before he was asked by the chair to bring his remarks to a close.

Finally Pippard, a member of the General Board, spoke in favour of the Board's proposals. He acknowledged that they concerned an extremely delicate matter, in which he had played some part, and, so he believed, not a very popular part.

As a result of the Senate House discussion, and subsequent discussions, the General Board concluded that the proposals were the most satisfactory solutions likely to be found.[64] They were aware that the solutions were a compromise, but no higher measure of agreement was likely to be attained, and that the protracted discussions had already damaged the University and the field of study at issue. They left to the new Committee of Management the task of determining the amount of space required, and the possibility of proposing new graduate posts if these were funded by the Oppenheimer fund alone, without any call upon University Education fund.

5. AFTERMATH

A new advisory committee for the Professorship of Biophysics was established[65] in February 1969: the only person common to both this committee and the previous one was Todd. Sir Alan Hodgkin[66] was elected Plummer Professor of Biophysics[67] in July 1969. He had previously held a Foulerton Research Professorship of the Royal Society and a Senior Research Fellowship of Trinity, and had won the Nobel Prize in 1963 for his work with Huxley[68] on cell membranes. His group of researchers "was a well-defined unit but it did not have a formal existence as a sub-department".[66] So Roughton's chair did indeed become one of Biophysics, albeit several years after Roughton's retirement.

When Hodgkin became Plummer Professor, Haydon moved to a new sub-department of Biophysics[19] in the Physiological Laboratory. Haydon's research interests, and his comments at the Senate House discussion, suggest that this was an entirely appropriate move.

Johnson[59] moved in 1970 to the Department of Biochemistry (headed by Professor F.G. Young[69]) until his retirement in 1984, after which he was given an emeritus position at the Cavendish by Sir Sam Edwards,[70] together with space for his experimental equipment. Such moves are relatively easy for theoreticians, who need simply to transport their pencil and paper, books, and (nowadays) computers. For an experimentalist, such as Johnson, they present considerable difficulties and disruption, with re-assembly and recalibration of equipment.

Ottewill had already left for Bristol in 1963, before the Council issued their 1965 report that led to the Senate House discussion. There he created what became the leading UK group studying colloidal suspensions. Activities included the synthesis of model colloidal systems and their characterisation by light scattering, neutron scattering, electrophoresis and osmotic pressure measurements. Ottewill subsequently became head of Physical Chemistry, Chair of the School of Chemistry and Dean of Science.[20]

In the Senate House discussion[1] Roughton stated that over 400 people had carried out research within the CUDCS, of which about half had gone into academic posts and the other half posts in industry & government. Leading research scientists in industry were particularly concerned about support for UK Colloid Science. An Industrial Physical Chemistry Committee was set up in 1969 by the Royal Society of Chemistry to explore how links between academic and industrial research could be encouraged by the Faraday Society.[71] The driving force behind this committee was Dr B.A. Pethica, who in 1953–1958 had been a Senior Assistant in Research in the CUDCS before moving to Unilever Research. He became head of Unilever's Port Sunlight Laboratory in 1965,[72] eventually leaving in 1976 to go to Clarkson College, New York. The members of the Committee, and particularly Pethica, persuaded the Chemistry Committee of the Science Research Council (which funded much of the UK academic research in the physical sciences) to set up a Colloid Science Panel in 1971. The panel had seven members from academia and two from industry, and had the object "To review the present status of the science of colloidal dispersions, both in academic institutions and in industry; to document the case for special support of this subject and to recommend methods of achieving its development".[73] Pethica would certainly have appreciated industry's need for colloid scientists. He also had to ensure that his laboratory was as well staffed as Unilever's laboratory in Vlaardingen, Holland, which could draw upon the strong tradition of colloid science in the Netherlands.

Johnson points out:[59,74] "Four out of the ten members of the panel were from the then suppressed Colloid Science department. The summary and conclusions represent a complete reversal of the actions taken in Cambridge and provides a useful pointer to the general scientific wisdom of specialised Nobel Prize winners."

Colloid Science survived in C.U. by the work not only of Johnson and Haydon, but also that of several other groups. Batchelor had first made his name in turbulence, but by the 1960s it was becoming hard to see how to make further progress[38] and he concentrated on editing and writing his *Introduction to fluid dynamics*.[75] In this he discusses Einstein's result for the viscosity of a dilute suspension of spheres. Problems with Einstein's analysis led to Batchelor's first paper on the fluid dynamics of suspensions, and his group in the Department of Applied Mathematics and Theoretical Physics became active in this field.

Mott had arrived as Cavendish Professor in 1954, and Philip Bowden[10] & David Tabor[76] changed the affiliation of their group studying friction between solid surfaces from the Chemistry Department to the Cavendish Laboratory in 1957. This enabled them to stay on the New Museums site when Chemistry moved to its new laboratories[15] on Lensfield Road (built as one of the conditions required by Todd if he were to move to Cambridge). Although much of Bowden & Tabor's work would not normally be classified as mainstream Colloid Science, mention must be made of the surface force apparatus,[77,78] which made direct measurement of the forces between mica surfaces. Subsequent developments by Israelachvili are documented in his monograph.[79]

Edwards[70] arrived at the Cavendish Laboratory in 1972 (though he was given leave of absence almost immediately, 1973–1977, to become Chair of the Science Research Council). He had already been introduced to polymer dynamics by Geoffrey Gee,[80] head of Chemistry in Manchester University, and at Cambridge he went on to develop the Doi-Edwards theory of entangled polymers[81] and establish a group working on statistical mechanics and soft matter.[82] An annual *Edwards Symposium* has been established to commemorate his work.

6. CONCLUDING REMARKS

Roughton put up a spirited and logically sound defence of his Department in the light of Todd's opinion that the CUDCS was in fact a second school of physical chemistry. Roughton saw problems looming as soon as Schulman resigned, and initiated a series of Annual Reports showing that the Department was very productive and emphasizing the Department's biological activities. Haydon & Ottewill's history of the Department[16] also emphasized links to biology, which was surprising in a publication aimed at mainstream chemists working in industry in the 1960s. Roughton had publicly advocated[83] as early as 1955 the creation of a special advisory committee for the CUDCS, containing "strong representation of relatively knowledgeable people from outside the university", similar to that existing for the Department of Geodesy and Geophysics, but his repeated requests fell upon deaf ears. Such a committee might have been able to convey to the University the scientific and industrial importance of colloid science. The modern University is far from adverse to Advisory Boards, which now exist for the Hamilton Kerr Institute, the

Judge Business School, the Museum of Zoology, and the Department of Land Economy, to name but a few.

Ottewill's departure to Bristol was detrimental to Colloid Science at Cambridge, but Cambridge's loss was Bristol's gain, and UK science would be in a sorry state if there were no top-class scientists outside Oxford & Cambridge. Ottewill's career clearly flourished at Bristol, as did Bristol as the UK centre of excellence for Colloid Chemistry during this period.

Cambridge learned from its mistakes with Colloid Science. In 1966 The Vice-Chancellor of the University received a letter from the UK Government's University Grants Committee suggesting that Cambridge's undergraduate teaching of agriculture should be discontinued. Various consultations and reports led to the redistribution of staff, either to the Department of Land Economy or to a new Department of Applied Biology. This was accepted by the University without debate.[84] In 1987 the General Board recommended the suppression of the Department of Applied Biology, and included details of what was proposed for each of the ten tenured academic staff, the Director of the University Farm and a Technical Officer, though there was no similar announcement for lower grade assistant staff.[85] Although this led to a discussion in the Senate House, the suppression went ahead without a vote.

Cambridge University now has many more administrators, including Human Resource managers, than in the 1960s, and its actions today would presumably be more professional (though I am in no position to confirm this).

It is clear that modern Cambridge would not hesitate to rename a laboratory in order to signify a change in direction. The BP Institute for Multiphase Flow, established in 2000 after a £21.65 million donation by BP,[86] was a multidisciplinary institute bringing together mathematicians, geophysicists, engineers, chemical engineers, physicists and chemists. It was announced[87] in 2022 that the Institute had been renamed the "Institute for Energy and Environmental Flows", to better reflect the scope of its research. One might wonder to what extent the timing of this announcement was linked to pressure from academics, and from students who occupied the institute and demanded an end to fossil fuel funding.[88,89]

I finish by quoting from Johnson's memoirs concerning the response of Johnson, Haydon & Ottewill when in 1963 they were read parts of the General Board reports: "we (three) together sent a memorandum to the General Board criticising not only the conclusions reached but also the secretive methods used in reaching them. Though receipt of the document was acknowledged, no reply was ever received. Looking back now on the episode after 30 years, I can scarcely believe that a supposedly democratic organisation could act in such an underhand and dictatorial manner."[59]

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APPENDIX: CAMBRIDGE GOVERNANCE

The governance of the University of Cambridge is based on a complex structure of committees which attempt to govern by consensus, rather than by decree. The Statutes and Ordinances of the University have evolved over time, with the last major revision in 2012–13. The brief (over-simplified) explanation below is based on the statutes[46] of 2024.

The **Council** is the principal over-seeing body of the University, with members elected from among the Heads of Colleges, Professors, other members of Regent House, and students. It is chaired by the Vice-Chancellor. In 1966 the equivalent body was the **Council of Senate**.

The **Regent House** consists of the academics, senior researchers and senior administrative staff of the University. They can vote for (or against) **graces** (i.e. proposals) initiated usually by the General Board, or the Council, or by members of Regent House itself.

The term **placet** (3rd person singular present indicative of the Latin verb *placere*, i.e. "it pleases") indicates a vote of assent. **Non placet** indicates a dissenting vote.

The **Senate** consists of all holders of the Cambridge MA degree and current members of the Regent House.

The **Senate House** is a large hall, situated in the centre of Cambridge, where gatherings, such as Degree ceremonies and Discussions, can take place.

The **Faculties** are bodies of academic persons, grouped by subject and divided into one or more **Departments**.

Each Faculty has a **Faculty Board,** consisting of elected members of the Faculty.

The Faculties are grouped into **Schools** of broadly similar disciplines (e.g. The School of the Physical Sciences). Each School has its own Council.

The **General Board** is responsible for management of the University's academic and educational policy. It reports to the Council. Its members are appointed by the Council and the various Councils of the Schools.

Suppression is the technical term used in the Statutes and Ordinances for the closure of a Department, Faculty or even a post such as a professorship or lectureship.

The **Cambridge University Reporter** is the University's journal of official business. It appears weekly during term time, with special issues devoted to major reports (e.g. financial accounts).

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Substantia

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