Nature, Aim and Methods of Microchemistry

Proceedings of the 8th International Microchemical Symposium

Organized by the Austrian Society for Microchemistry and Analytical Chemistry
Graz, Austria, August 25–30, 1980

Edited by H. Malissa, M. Grasserbauer, R. Belcher

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PREFACE

This proceedings volume of the 8th International Microchemical Symposium contains the plenary and keynote lectures delivered at the conference.

Besides basic and historic aspects the following major topics are covered:

"Microchemistry in Arts and Archeology"
"Microchemistry in Life Sciences"
"Microchemistry in Environmental Sciences"
"Microchemistry in Material Sciences"
"Instrumentation, Methods and Automation in Microchemistry".

The papers show the present state of microchemistry and the development of this field since the pioneer days of Fritz Pregl and Friedrich Emich. Today microchemistry is a different science as compared to the Pregl and Emich days, for it combines many disciplines like chemistry, physics, mathematics, informatics, biology and does not only mean microanalysis - even if it is still predominant and the best tool for elucidation of the microcosmos.

Due to this development modern microchemistry plays an important role in science and technology. It had been the intention of the Scientific Executive Committee to demonstrate this at the 8th International Microchemical Symposium with the goal to encourage interdisciplinary communication and stimulate discussion.

April 1981

H. Malissa, Vienna
M. Grasserbauer, Vienna
R. Belcher, Birmingham

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NATURE AND AIM OF MICROCHEMISTRY -
AN INTRODUCTION TO THE 8TH INTERNATIONAL MICROCHEMICAL SYMPOSIUM

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Abstract. In order to stimulate the discussion for clarification of the term "Microchemistry", and what are its nature and aim some thoughts and examples of basic interest and practice are presented, without claiming a complete depiction.

It gives me a feeling of exaltation that we are able to meet again, thirty years after the first International Microchemical Symposium - organized by the same society as today - and for the third time in this town of great microchemical tradition. Some of us may feel the spirit of this place, where 60 years ago F. Pregl and his antagonist F. Emich laid down what is generally meant by the term "Microchemical School of Graz". But we must not forget that this is also the town where L. Boltzmann evaluated 100 years ago, the famous thermodynamic principles which are ruling not only chemistry, but also physics and information.

It is not my intention to go into the history of microchemistry; and I am not claiming microchemistry as an Austrian "invention". We know only too well that p.e. 300 years ago R. Hooke, Fellow of the Royal Society, published his famous book on Microchemistry, entitled "Micrographia" and furthermore that French as well as German, Russian and Dutch scientists were deeply involved in microchemistry some 150 years ago. A look at the exhibition will show you some more details.

Up to now - it seems to me - microanalysis stands for microchemistry and has already become a synonym for it. So - apparently - , it is really high time to try to clarify the situation and to try to evaluate what is really meant by the term "microchemistry", and what is its nature and its aim.

It is interesting to note that there are no problems when one speaks about microphysics and of the microcosmos in general, but as soon as the word "microchemistry" appears, nearly everyone thinks of "microanalysis" only.

Today we feel a strong tendency to amalgamate again philosophy and science, as was usual in earlier times of human search for knowledge. We know very well that pure philosophy, pure science and pure technology without any reciprocity and without a high amount of reflection to ethics leads us towards a dangerous situation - either running out of goods or merging in a meaningless and, moreover, hopeless world. Prof. Frankl's lecture will give you some impressions.

This is certainly not the place, and time is too short for going into the aspects of "controlled research", but the temporary world-wide discussion, about p.e. gene technology or extensive atomic research, forces us to establish new ways for research patterns, whereby the framework will be the dialogue: scientific research ↔ ethic reflection via proper assessment studies. That the best starting-point with the lowest probability of destruction of our environment would be certainly the work at the microscale level. This is quite clear and does not need further explanations.

As long as everything has been done and is done on an easily controlled "microscale", as long as things went well and new wisdom could be gained; but as soon as "larger" amounts become involved, beyond financial interest, political and even military aspects are often the dominating factors to further research - and discrimination begins.

First of all, let me make a statement:
"Microchemistry exists and plays an important role in our life and research work, regardless if we accept this or not. The major problem is to define its border lines".

It is just a question of our philosophy, what rank, which place and what dimensions we assign to microchemistry. Since Einstein gave us the fourth dimension, nature can have different pictures depending on the state of motion of the "observer". This principle makes every definition very difficult or even senseless. To define microchemistry is as senseless as the definition of inorganic and organic chemistry, because it is not the object which makes the problem, it is the subject. To define microchemistry is as difficult as it is to define "life". Very often it is more or less a personal problem to follow exact rules and dimensions, we are always attempted to use and to include some "private" fixation of limits. The thinking and working in thousands of light-years and mega-tons as well as in fractions of seconds and grams has forced us to scale units in over 24 decades and more and more it makes no problems for us to think and to work in a world of pico-grams.

Year by year rockets are sent into the space to "look" behind the "world" of our planet and in two years (1982) again a Spacelab will be sent into the orbit with apparatus of the Technical University of Graz on board. Minute chips are built in and the circuits and pieces of detectors are as small as 2 x 2 mm transmitting decades of signals. On the other hand transplantations and implantations under the microscope of very interesting biological minute bodies are going to lose their reputation of being impossible and worthless.

In order to understand the nature and aim of microchemistry we have to include in our considerations some philosophical momenta not only in respect to "macro" and "micro", but also to "classic" and "modern" as well as the meanings and definitions of terms like canonical systems and ensembles, causality and so on. And here starts what is meant by amalgamation of philosophy and sciences.

Both in thinking and in writing we can establish and model every system with every canonical ensemble, as large or small we like. In reality we are bound to nature - and the verification of an axiom or theory - we may better say the falsification of it - can only be done by observations and measurements. This means in first instance the careful elaboration of measurement of differences of thermodynamical and kinetics parameters of the initial and final state of our stepwise scaled down system until the mean free pathway is reached. These borderlines will designate the real nature of microchemistry. This means further the broad use of micrurgy and miniaturization of tools as well as volumes and a heavy fight against the ratio volume over surface will accompany the perceptibility of microchemistry in practice.

From the first formation of minute amounts of substances in small volumes to the coacervation of molecules to larger units, the whole evolution process is bound to thermodynamics, especially to entropy, and chemical kinetics.

The idea of entropy has been generalized and built into nearly every branch of sciences. In physics as well as in chemistry, biology, cosmology and also in information theory down to linguistics.

But the roots of this concept are in the physics of macroscopic thermodynamic phenomena - in the heat engines of the 18th century. The development has led us to an extended Boltzmann-Planck formulation in the generalized form of

$$\dot{S} = k \cdot \log W (\bar{E}, \bar{N}, \bar{V}, \bar{\beta})$$

where the thermodynamic weight W is now defined to the number of microscopically specified possible states, corresponding to a given macroscopic equilibrium state of the system under consideration ($\bar{E}$ = internal energy, $\bar{N}$ = average particle number, $\bar{V}$ = volume and $\bar{\beta}$ = average values for their internal state parameters). As M. Harrison pointed out in his consideration of the entropy concepts in physics there is one important difficulty in the application of the second law to our universe as a whole. It is clear from everday experience and observations that the universe as a whole is not in a state of thermodynamic equilibrium. And yet as a single closed system one might expect it to have reached equilibrium long ago. The temptation to regard the observable part of the universe as a very large fluctuation in a system in equilibrium as a whole can be resisted by realizing that comparable non-equilibrium conditions supporting biological development and human observers can occur on a smaller scale with even greater likelihood, because there is a greater probability for a suitable fluctuation in the structure of smaller systems, for it contains far fewer degrees of freedom than the galaxy.

Here the selection of microsystems of a proper canonical ensemble will produce a broad field for research and with its aim a lot of discrepancies between calculated and measured values of real systems can be cleared off and eventually new wisdom gained.

As far as chemical kinetics is concerned even more complexity may occur. Regardless which theory is our favourite, collision - or activation theory, particle number and volume, this means particle and flux density, are the dominating factors.

In every case we have to consider the ratio N/V very carefully because here again is one of the keys to the nature of microchemistry.

It is of the greatest basic interest to learn more about the compatibility of calculated values in reference to measured data of fixed particle number by lowering the volumes to the smallest system possible at a given temperature. It is simply the problem to find for each chemical system the limit where the probability of the occurrence of a chemical reaction changes from "one" to a significant lower number.

From the practical point of view the borderlines of microchemistry are not only where the smallest number of reactants are present in the smallest volume to be handled for a giving equilibrium-condition, but even more where the physical properties change drastically with the volume. From this point is the smallest amount meant which can be handled in the vicinity of the equilibrium-condition. In 1950, Benedetti-Pichler, the well-known co-worker of Emich and his ambassador to U.S., had already mentioned that about 60.000 molecules are necessary to assure chemical reaction proceeding the same way as larger amounts. Taking a mean molecular weight of 100 p.e. leads us to the masses of $1,7 \cdot 10^{-16}$g. But it is a tremendous difference having this amount dissolved in 100 ml or 100 µl. How sensitive the ratio N/V is, can easily be demonstrated (for gases) by the formula for collision frequencies.

To learn more about the nature of microchemistry we must give attention to morphogenetic principles and we should do more research on conservative and dissipative reaction mechanisms. Whilst the former is (more or less) under consideration, also on the microscale is the latter not in the files of larger investigation programs.

We have only to think of homogeneous oscillating reactions of the Belousov-Zhabotinskii-type to be performed in the smallest volume, also, not only at low concentrations as has been done up to the present. The field of research on microchemical oscillators is still open and waiting for elucidations.

A practical example of the aims of microchemistry is the advanced research activity on the lifetime and chemical surface reactions of droplets of the order of 1 - 2.000 µm in diameter. T. Novakov and his school in Berkeley are doing a great deal of work in this respect and we will hear something about it in the session of environmental analysis of this symposium. But it is realy interesting to learn from relative simple experiments - microdroplet on a very thin quarz fibre under remote condition - that the lifetime of a droplet with about 10 µm diameter covered with soot and surface reactants can have at r.h. of 80 % a lifetime of more than 17 hours and is about 10.000 times larger as somewhat larger droplets. What this means for the environmental control activities can easily be imagined.

The aims of microchemistry are too many and cannot be demonstrated briefly; the plenary and keynote-papers will give you a very good impression. But in general, the aim of microchemistry is the elucidation of all the forces, particles and arrangements at the starting point of all the compounds and bodies which built up our macroscopic world. Microchemistry is not as "weak" as we may believe, we are only too diffident to arrange the analytically found data to a canonical system and to articulate our findings.

We will not make any progress in our efforts of so-called better life and worthwhile world, if we do not give more attention to the elucidation of microprocesses. The formation and conversion of pollutants p.e. cannot be studied without considering micro-heterogenic catalysis. We are able today to collect and to study particles as small as 0,1 μm at very low sampling rates (that means with very good time resolving), and we are going to elucidate the reaction mechanism in spots of less than 0,1 mm; and it is one of the other aims of microchemistry to give guidance in this broad domain of research activity on life and material science.

We know that small amounts of masses have other physical properties p.e. surface-tension of droplets - is quite different as flat surfaces. The behaviour of whiskers as an example of what microchemistry and microtechniques can do has influenced the solid-state technology to an enormous extent. Small crystallites have always lower melting-points and higher heats of combustion, etc. The study and the interpretation of these phenomena of the micro-range are still a wide field of activity and need a vast amount of often very sophisticated instrumentation. As a general rule we can say: the smaller the amount or volume to be investigated the larger (and more expensive) the machinery. And what we are interested in is not as much trace-chemistry (chemistry at very low concentration), but microchemistry, where beyond chemical parameters, physical forces are of great importance. This means, the main aims of microchemistry lie in studying the problems:

a) Is there an overlapping and moreover an overruling of physical laws over chemical laws in reaction dynamics in building up compounds and phases, and

b) if yes, where are the borders as far as size of reaction volumina and masses are concerned.

This short introduction to our meeting is not to be considered as the explanation of microchemistry, but rather a trial to open our mind in this respect.

We have invited outstanding scientists from various fields of science in order to enlighten different fields of microchemistry and hopefully by the end of this symposium you will be better informed about this domain. You must not forget that the best teacher and the best scout in finding the proper way to relatively unknown fields is always the analysis. Therefore microanalysis will be not only one of the most important branches in microchemistry, but serves also as a forerunner of new arrangements of very great simplicity as well as sophistication in handling small amounts and volumes. What has to be done in order to obtain a better elucidation of what microchemistry really is - is the conversion of data, not only to the composition of small amounts of material, but more to the physico-chemistry of reaction mechanisms especially in the range where the probability is much less than "one". The field of "uncertainty of chemical reaction", as F. Emich has named this area 70 years ago and where research has nearly stopped. Now we have to go in again to find out the borderlines mentioned before.

HISTORY OF MICROCHEMISTRY TILL 1945

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Abstract. Microanalysis and macroanalysis today. Beginnings of microscopic identification of compounds. Boricky's, Haushofer's and Behrens' work. Emich and the development of the Austrian school of microchemistry. Organic qualitative and quantitative microanalysis. Microtitrimetry. Catalytic ultramicroanalysis. Development of colorimetric and photometric determinations. Birth of activation analysis and chromatographic microanalytical methods.

The extensive spreading of microchemistry in recent times has created a conceptual uncertainty both in methods and in applications.

Little by little, all chemical analysis turns into microchemistry, rightly speaking into microanalysis. In fact, the confusion started with the term itself, namely that the name microchemistry was adopted long ago, although what is meant is microanalysis. Probably the term microchemistry was derived from the abbreviation of the title of Raspail's book "Essai de chimie microscopique" which appeared in 1831. Microscopic chemistry: microchemistry. Later, the classicists of microchemistry, among others Emich, clearly defined microchemistry as the methods using micro amounts of sample, quite precisely amounts of sample below 0.01 g. Thus the term does not include methods in which micro amounts, that is, below 0.01%, of a component can be determined. However, this distinction is not used subsequently in the literature. Methods aiming at the determination of traces are frequently named microchemical methods. Even the various microanalytical publication series like Hecht-

Zacherl and Benedetti-Pichler devote whole volumes to methods of trace analysis. In fact, it is frequently difficult to make a distinction. Practical science should always contemplate the aim, the usefulness and should not trouble about the coherence of some definition. I believe this to be valid for human society as a whole, in all its manifestations.

It appears that nowadays macroanalysis is applied only in industrial and agricultural routine analyses, in scientific analytical chemistry microanalysis and trace analysis gradually became practically the only methods. The subject to be discussed here is scientific analytical chemistry, the discipline which is the servant of other scientific disciplines: ancilla scientiarum.

In the circular announcing the publication of the first journal for analytical chemistry, the Zeitschrift für analytische Chemie, Remigius Fresenius wrote in 1861: "Ohne Mühe läßt sich nachweisen, daß alle großen Fortschritte der Chemie in mehr oder weniger direktem Zusammenhang stehen mit neuen oder verbesserten analytischen Methoden. Den ersten brauchbaren Verfahrungsweisen zur Analyse der Salze folgte die Erkenntnis der stöchiometrischen Gesetze, die Fortschritte in der Analyse der anorganischen Körper fanden ihren Ausdruck in den immer genaueren Äquivalentzahlen, der genauen Methode zur Bestimmung der Elemente organischer Körper folgte der ungeahnte Aufschwung der organischen Chemie, die Spektralanalyse führte sofort zur Entdeckung neuer Metalle etc. Die Entwicklung der analytischen Chemie geht daher der Entwicklung der gesamten chemischen Wissenschaft immer voraus, denn wie frisch gebahnte Wege zu neuen Zielen, so führen bessere analytische Mittel zu neuen chemischen Erfolgen. Eine ähnliche bedeutende Einwirkung verbesserter analytischer Methoden gibt sich auch bei den anderen Wissenschaften und Fächern, welche mit der Chemie verwandt sind, aufs Deutlichste zu erkennen. So wurden, um nur einige Beispiele zu erwähnen, die Löthrohrreaktionen bald wichtige Hilfsmittel zur Unterscheidung der Mineralien, so führte die Entwicklung der Analyse bald, infolge der hierdurch möglichen Prüfung der Arzneimittel, einen großen Aufschwung in der Pharmazie herbei, so folgte der Entdeckung der Alkalimetrie, der Chlorometrie und anderer rasch ausführbarer, namentlich maßanalytischer Methoden bald der solide Gebrauch, chemische Waren von bestimmten, verbürgten Gehalten in den Handel zu bringen, so führten die vereinfachten Methoden der Stickstoffbestimmung und Aschenanalyse rasch zu einer Reihe der wichtigsten physiologischen und agrikulturchemischen Wahrheiten, so erhielt die Untersuchung menschlicher Ausscheidungen für die medizinische Diagnose erst Wert, als die vereinfachten analytischen Methoden eine rasche Ausführung ermöglichten, so wurden die genauen Methoden zur Ermittlung von Giften, Blutflecken usw. bald die gefährlichsten Feinde der Verbrecher. Die analytischen Methoden