Published in:
P. Morris (ed.): *From Classical to Modern Chemistry: The Instrumental Revolution*,
Cambridge: The Royal Society of Chemistry, 2002, pp. 188-211.

The Impact of Instrumentation on Chemical Species Identity

From Chemical Substances to Molecular Species

Joachim Schummer

1. Introduction: The ontological issue of identity

Every science is about certain objects or entities. Talking about objects in an unambiguous and constant way requires a notion of identity. Usually, scientists take that for granted or implicitly use a certain notion without further reflection. The notion of identity thus becomes part of their habitual ontological commitment. Sometimes, however, ontological issues emerge in the forefront of scientific research, such as the well-known ontological problems of quantum mechanics. While philosophers of science have much debated the quantum mechanical issues, every classificatory science is more involved in ontological issues than physics. That is particularly true concerning chemistry, since chemists are deeply involved in classificatory problems. Just imagine the tremendous efforts that were necessary to distinguish carefully between millions of substances today, most of them being white powders indistinguishable to the naked eyes.

A lot of crucial episodes in the history of chemistry are related to identity issues. Take for instance the alchemical quest for making precious metals such as gold. Many skeptics argued that, for ontological reasons, artificial gold cannot be the same as natural gold; even if all empirical properties are the same, artificial and natural substances are strictly distinct. They referred to a non-empirical concept of substance identity, for which they found support in Galen's and Avicienna's odd interpretation of Aristotle's distinction between natural things and artifacts.[1] A second, and related, example is the debate between vitalists and anti-vitalists in the nineteenth century. Berthelot's enormous efforts in synthetic organic chemistry was to provide rich material evidence for his anti-vitalist claim that there is no ontological difference between natural and artificial organic substances.[2] A third example, which eventually paved the way for the modern concept of elements, comes from eighteenth century Swedish mineral chemistry. Against the prevailing assumption that nickel, cobalt, and manganese were modifications or mixtures of the few accepted metals, Axel Cronsted and Torbern Bergman argued that they must be considered as distinct metals, because they possess distinct and constant properties and can-

---

[1] *Cf.* R. Hooykaas: 'The discrimination between "natural" and "artificial" substances and the development of corpuscular theory', *Archives internationales d'histoire des sciences*, 1 (1947/48), 640-651; W. Newman: 'Technology and alchemical debate in the late middle ages', *Isis*, **80** (1989), 423-445; B. Obrist: 'Art et nature dans l'alchimie médiévale', *Revue D'Histoire des Sciences*, **49** (1996), 215-286; J. Schummer: 'The Notion of Nature in Chemistry', in: *Proceedings of the Fourth Summer Symposium on the Philosophy of Chemistry and Biochemistry, Poznan, 7-10 August, 2000*, ed. by E. Zielonacka-Lis & P. Zeidler, Poznan 2001 (forthcoming). For a reinterpretation of Aristotle's distinction, see J. Schummer: 'Aristotle on Technology and Nature', *Philosophia naturalis*, 38 (2001), 105-120.

[2] *Cf.* C.A. Russell: 'The Changing Role of Synthesis in Organic Chemistry', *Ambix*, **34** (1987), 169-180.

not be made from the other metals.[3] As we will see later, Bergman first formulated and consistently applied a rather modern concept of substance identity. The most important example, however, is the change of the concept of elements. What was formerly considered a change of substance identity in Aristotelian terms, was later simply a change of state of aggregation, say from ice to liquid water, retaining substance identity.[4]

Let us turn now to philosophical formulations of the concept of identity. According to the famous law of Leibniz, two entities (x and y) are identical, if and only if they possess exactly the same properties (ϕ):

$$x=y \equiv \forall\phi\{\phi(x) \equiv \phi(y)\}$$

Until today there has been much debate in philosophy about which (kind of) properties shall be considered in this definition. A strong (anti-Leibnizean) tradition prefers a version of the Principle of Identity, according to which all properties, including space-time coordinates, must be the same to hold identity, *i.e.* numerical identity. Others distinguish between so-called 'intrinsic' and 'extrinsic', 'pure' and 'impure', and so on properties to derive various weaker concepts of identity. In the present context, we need not bother much about these sophisticated distinctions, mainly because they are irrelevant for the question of identity in chemistry and tailored to some other specific areas (as philosophers are used to ignore chemical issues). Instead, we can confine ourselves to the more liberal concept of relative, qualitative, or species identity. If we take material samples as the primary entities of chemistry, chemical species identity can be defined in terms of properties that are regarded as essential for the sameness of chemical species. Two material samples are chemically identical if and only if they possess all the same essential properties. If they differ in only a single essential property then they belong to different species.

The whole issue of species identity in chemistry now comes down to the question of which properties count as chemically essential. The problem is far from being trivial, however. As we will see later, the scope of essential properties even has an impact on what we count as a chemical entity. Furthermore, as the identity issue is an ontological problem, it should be well distinguished from the epistemological problems if and how chemical identification can actually be achieved. Chemical identification presupposes a concept of species identity. Such a concept is also presupposed when a sample of a new species is found or produced because the novelty must be substantiated by establishing or fixing the identity of that species in terms of its essential properties.

---

[3] *Cf.* J.W. Llana: 'A Contribution of Natural History to the Chemical Revolution in France', *Ambix*, 32 (1985), 71-91 (77). Of course, the critical view on the received notion of elements was already prepared by Boyle.

[4] There is a wealth of other prominent historical examples of identity issues in chemistry. To mention just three more: (1) In the late sixteenth century, the ontological status of fire, as one of the Aristotelian elements, was called into question and remained so for centuries. The ontological issue was whether fire is a substance at all, identical with itself, or an attribute or a state of other substances. (2) Another example is the ontological status of phlogiston as discussed in the eighteenth century. Different experiments proved either an earth-like (Stahl), an air-like (Cavendish), or a fire-like (Rouelle) nature, all of which could hardly be reconciled with one self-identical material substance. The pre-nineteenth century history of the chemical elements or principles is particularly rich in variants of ontological status, from mere 'explanatory entities', to property-conferring principles and reified material substances; for more details see J. Schummer, *Realismus und Chemie*, Würzburg, Königshausen & Neumann, 1996, chapt. 4.3. (3) The early nineteenth century debate between Berthellot and Proust (and others) about the difference between homogeneous substances with definite and with varying composition depended on the question whether definite composition is considered essential for chemical species identity or not. On this and related issues in mineralogy see R. Hooykaas 'The Concept of "Individual" and "Species" in Chemistry', *Centaurus*, 5 (1958), 307-322.

The concept of species identity, while being prior to epistemological questions, need not be fixed once for ever. In contrast, as we will see, the concept has changed several times in the history of chemistry. Since the present paper focuses on these changes, it is not about ontology in the received view but about the ontological attitude of chemists. Moreover, since there has not been an explicit discourse about the concept of species identity in chemistry, the ontological attitude of chemists must be derived from their actual practice as reported in the literature. To that end, I will mainly drawn on how chemists have established the identity of new species in synthetic chemistry,[5] and occassionally on their practice of species identification.

The main topic of the paper is the impact of twentieth century spectroscopic instrumentation on chemical species identity. In order to understand the tremendous change, we need to consider first the starting point, *i.e.* how species identity was defined and determined in classical modern chemistry.

2. Species identity in classical modern chemistry

2.1 Historical steps towards canonical substance characterization

I would like to use the term 'classical modern chemistry' for a scientific approach in chemistry that was to overcome gradually both metaphysical and mere observational attitudes in favor of experimental and operational approaches, before the rise of spectroscopic methods. As the introductory examples have already illustrated, chemistry was largely bound to a metaphysical concept of substance identity until the late eighteenth century, if not later in some regards. Whatever observational properties two material samples had in common, they could be considered different because of different underlying metaphysical principles. We should not forget that such mistrust of observational properties was well founded. Two material samples may look the same, but turn out to behave quite differently in certain contexts. On the other hand, two samples may have a different appearance (*e.g.*, because of impurities or different modification forms) but behave in the same way in chemical contexts.

The classical modern approach to substance identity was, as far as I know, first formulated and consistently applied by Torbern Bergman. He defined substance identity in terms of composition which was operationally related not only to experimental analysis but also to experimental synthesis: "In investigating the principles of a body, we must not judge them from a slight agreement with other known bodies, but they must be separated directly by analysis, and that analysis must be confirmed by synthesis."[6] As Llana has pointed out, Bergman clearly disregarded the philosophical elements for the purpose of substance identification. Instead, composition had to be formulated in terms of simple substances, *i.e.* the outcome of final experimental analysis which then must be the starting point of experimental synthesis. As a central part of the so-called chemical revolution, Bergman's approach, which was basically restricted to minerals, was later enlarged by Lavoisier and others and put on the sound basis of chemical elements as the final products

---

[5] I intentionally exclude natural products because their origin provides additional links for establishing species identity.

[6] T. Bergman, *Opuscula physica et chemica* (1779-80); quoted from Llana 1985, p. 78.

of chemical analysis.[7] It was up to the next generation then to develop experimental standard procedures for elemental analysis particularly of organic substances,[8] and it took even more generations to establish the required synthetic capacities for organic substances.

In Bergman's as well as many earlier chemical writings, we find a more or less implicit notion of *purity* of substances. If chemists spoke of substance identity, be it in the metaphysical or in the chemical sense, they usually related this concept only to 'pure substances'. Surprisingly, there is very little known about the history of that most fundamental chemical concept.[9] However, we have good reasons to believe that the standard methods for purifying liquids and solids remained roughly the same at least since the mid eighteenth century, mainly distillation, sublimation, and recrystallization. Carl Scheele, for instance, constantly used solubility and crystal form or boiling point as qualifying properties of his reagents,[10] which suggests that he routinely recrystallized or sublimed his solids and distilled his liquids. And since there is, for basic reasons, no way to define the concept of substance purity other than by referring to operational methods of purification,[11] we may assume that our concept of purity was already (implicitly) well established in the eighteenth century.

Hence, purified material samples were the objects for which species identity was determined, and this was done by providing the elemental composition based on both experimental analysis and synthesis as well as by some auxiliary properties. That approach remained basically the same until about 1950. Let us see now how chemists usually characterized, and thereby fixed the identity of new chemical substances in the first half of the twentieth century.

2.2 Canonical characterization of new substances

Browsing through chemistry journals of the first half of the twentieth century reveals an obviously schematized characterization of new substances that one is justified in speaking of a canonical form. The canonical form of classical modern chemistry consists of six categories:

1) detailed description of preparation from starting materials, including purification method (distillation, recrystallization) and yield;
2) results of elemental analysis including empirical formula (occasionally molecular weight);
3) melting point or boiling point (including pressure if vacuum distillation is applied);
4) visual characteristics (crystal form, color);
5) solubility in various solvents;

---

[7] R. Siegfried, B.J. Dobbs: 'Composition: a Neglected Aspect of the Chemical Revolution', *Annals of Science*, **24** (1968), 275-93.

[8] *Cf.* F. Szabadváry, *History of Analytical Chemistry*, London, Pergamon, 1996, chapt. IX. For a more detailed study of analytical chemistry of that period with emphasis on the German laboratory practice and education system see E. Homburg: 'The Rise of Analytical Chemistry and its Consequences for the Development of the German Chemical Profession (1780-1860)', *Ambix*, 46 (1999), 1-32.

[9] *Cf.* W.H. Brock, *The Fontana History of Chemistry*, London, Fontana, 1992, pp. 173-176, 688. Szabadváry (1966, p. 150f.) mentions an early textbook of analytical chemistry from Labadius (1801), with "the earliest records of standards methods used for testing the purity of analytical grade reagents […] in many cases very similar to present day methods."

[10] Brock 1992, p. 174.

[11] *Cf.* J. Schummer: 'The Chemical Core of Chemistry I: A Conceptual Approach', *HYLE–International Journal for Philosophy of Chemistry*, **4** (1998), 129-162 (136-139).

6) some exemplary chemical reactivities.

Let us check now if this is an adequate list of properties to fix the chemical species identity.[12]

Surprisingly, from a systematic point of view, neither one nor all of these properties suffice to fix chemical species identity in an unambiguous way. Imagine you have a million data sets of that kind and want to decide if each constitutes a distinct chemical species. Given the coarseness of qualitative properties 4-6 and the limited precision of quantitative data 2 & 3 as well as the possibility of isomers, we would expect to find many doublets and triplets in a database of distinct chemical substances. Moreover, since there can be more than one way to produce a certain substance, property 1 would make us distinguish substances that we otherwise consider to be the same. From a pragmatic point of view, these problems might have been negligible in the nineteenth century, but not so in the mid twentieth century when nearly a million chemical substances were known.

From a systematic view point, the problem is even more grave, because the number of physical and chemical properties is unlimited.[13] Thus, if we extend the canonical set and consider all physical and chemical properties as essential properties, there are infinitely many properties to be considered. Two samples belong to the same chemical substance, if all of their essential properties are the same. If there is only a single essential property in which they differ from each other they belong to different chemical species. Hence, since it is practically impossible to determine infinitely many properties, we can never reach the conclusion on a logically sound basis that two samples really belong to the same chemical substance. That is to say, all identity claims in chemistry, based on an open set of essential properties, are necessarily only provisional.

As far as I know, Wilhelm Ostwald was the only chemist who fully realized that this problem challenges the fundaments of chemistry. The way he tackled the issue on the first page of his *Grundriß der Allgemeinen Chemie* is telling. He simply invented a first law of nature (*Naturgesetz*): "If two substances correspond in some properties, then they correspond also in all other properties"[14] Ostwald should have known that this is too good to be true. Given a finite level of measurement precision and a certain range for 'some' quantitative values of material properties, simple mathematics tells us how many possible substances can be distinguished by these properties; and how many doublets we should expect among a given number of substances. Even if we refer to the 'qualitative' chemical properties, the case of different isomers that correspond in many but not all properties disproves Ostwald's 'law of nature'. The 'law' was simply an anachronistic reference to the canonical form of substance characterization. By the time Ostwald formulated his law, the mere quantity of known chemical substances had already practically undermined such simplistic solutions.

---

[12] It should be noted that this is how chemists actually characterized their new substances and thereby provided the only information for substance identification to colleagues. For a more enlarged list with stronger emphasis on chemical properties, see Marcelin Berthelot's suggestion how to identify natural with artificial substances in his *Chimie Organique fondée sur la Synthèse,* Paris, Mallet-Bachelier, 1860, vol. II, pp. 778-86 (reprinted: Bruxelles: Culture et Civilisation, 1966).

[13] *Cf.* J. Schummer: 'Towards a Philosophy of Chemistry', *Journal for General Philosophy of Science*, 28 (1997c), 307-336. Since all material properties are context dependent, variation of the context generates new properties; *e.g.*, variation of pressure conditions generates different boiling points. While these points may be summarized in a function, as one complex property, chemical properties resists such mathematical strategy. By variation of reaction conditions including reaction partners, combinations of reaction partners, and so on, one can generate indefinitely many properties.

[14] "Wenn zwei Stoff bezüglich einiger Eigenschaften übereinstimmen, so thun sie es auch bezüglich aller anderen Eigenschaften" (W. Ostwald, *Grundriß der Allgemeinen Chemie*, 3rd edn., Leipzig, Engelmann, 1899, p. 1).

In fact, chemists did not trust their canonical characterizations, let alone Ostwald's 'law'. This is well documented in every chemical paper where *practical substance identification* was required on a safe basis. If chemists wanted to prove that the outcome of a new reaction was chemically identical with an already known substance, they did not rely on comparing characteristic properties. Until the 1960s, instead of comparing data, the usual way to prove identity with an 'authentic' substance was by mixing the two samples physically and examining mixing effects, like melting point depression. For that purpose, either the 'authentic' substance was reproduced according to the literature or even a sample was physically handed over from a colleague, which was usually acknowledged in the paper. That is to say, chemist actually relied on an *operational concept of substance identity* based on mixing samples instead of comparing essential properties.

We may conclude that the canonical characterization of new substances served to fix chemical species identity only within a certain context. First of all, it allowed chemists to identify a chemical substance among the other reaction products of the described preparation procedure. Beside that, chemists familiar with the corresponding substance classes and types of reaction might have used more or less implicit knowledge that helped them grasp substance identity by tacitly excluding implausible candidates. The specific form in which this knowledge had become explicit was chemical structure theory, an ingenious approach to tackle the chemical identity issue.

2.3 Support from chemical structure theory

Today we are inclined to consider chemical structure theory as the central step of entering the microcosm of molecules and atomic structure. However, such a view tends to overlook the specific chemical problems that structure theory helped to solve. As regards the problem of chemical species identity, structure theory was an invaluable means, particularly in the realm of organic chemistry where the rapid proliferation of substances had caused enormous problems.

Let us first recall the identity problem. Since there are indefinitely many characteristic properties in which chemical substances can differ, one has to determine and compare indefinitely many properties of two samples in order to prove their substance identity, which is impossible. Hence, all identity claims in chemistry based on an open set of characteristic properties are necessarily only provisional.

How did chemical structure theory help to solve the identity problem? The fundamental (either metaphysical or methodological[15]) assumption of structure theory was that there is exactly one characteristic chemical structure for every chemical substance. By that assumption, chemical species identity was transferred to a theoretical level, *i.e.* substance identity should correspond to structure identity and *vice versa*. As a consequence, experimental structure determination of a substance was at the same time the fixing of chemical substance identity.

Of course, chemical structure determination was also made with the help of empirical properties, first of all chemical properties. The ingenious way to determine substance identity via structure determination consists in the *careful selection of a few chemical properties among the infinitely many characteristic properties.* There are neither definite selection rules nor a fixed canon of properties, like the canonical characterization. Instead, for each

---

[15] For a discussion of the status of that assumption and the problems arising from the metaphysical misinterpretation by dialectical materialists with regard to the 'hot topic' of resonance structures, see Schummer 1996, pp. 253, 279ff.

chemical substance it is up to the chemists to select and find those chemical properties that allowed an unambiguous assignment of a certain structure. Sometimes only a few reaction properties are necessary to infer the structure of a new substance from already well defined others. In other cases, several research groups worked for years on the structure determination of a single substance, by devising sophisticated steps of controlled decomposition, partial resynthesis, or modification. That made structure 'elucidation' an enterprise which filled many chemists with a deep intellectual satisfaction.

With the help of structure theory, the number of properties for fixing substance identity shrank from infinity to a carefully selected set. Moreover, substance identification no longer required the physical presence of a reference sample, nor the comparison of physical data. It only required the comparison of two structures obtained by independent procedures of structure determination. When the first complete records of known structures were set up and ordered in a systematic way, chemists could easily check whether their new products were really new or identical with already known substances.

One might wonder why the canonical characterization of new substances remained an obligatory part in every chemical paper. For one thing, chemical structure determination only gradually became a constitutive part of chemical papers, and only in organic chemistry. You can even find papers in the 1950s in distinguished organic chemistry journals like *Liebig's Annalen* with careful listings of canonical characterizations, but without any constitutional formula. I assume that for many chemists chemical structure elucidation remained too 'hypothetical' to become the exclusive basis for substance identity. Over and above that, parts of the canonical characterization have their own rights. First, they present the 'uninterpreted' experimental properties on which the structure determination is based. Secondly, they meet the laboratory needs of relative substance identification within experimental contexts. Finally, the preparation description is an indispensable detail that allows other chemists to reproduce the results as well; and as such, it is a central condition of a scientific report.

2.4 The social side of substance identity (claims)

If I am right that the production of new substance has constantly been the central chemical activity during the past two centuries, as I have argued elsewhere,[16] then the issue of substance identity has also an important social side that has probably been the driving force for all solutions. For ordinary working chemists – not for the heroes of chemistry – the production of new substances is their main contribution to the progress of chemistry. Unlike other scientists, chemists are not only authors of ideas and papers, they are also authors or creators of new kinds of material entities. However, you need to determine first the identity of a certain entity, before you can claim certain rights. Thus, fixing the identity of a new substance means at the same time making an unambiguous claim to an original contribution.

Everybody familiar with the history and sociology of priority claims and struggles in science[17] knows how important clear rules are for the progress of science. This is particularly true if we have to deal with hundreds of thousands or even millions of such claims,

---

[16] *Cf.* J. Schummer: 'Scientometric Studies on Chemistry I: The Exponential Growth of Chemical Substances, 1800-1995', *Scientometrics*, 39 (1997a) 107-123. Note, for instance, that on the average every chemical paper abstracted today by *Chemical Abstracts* reports on the synthesis and characterization of 1.7 new substances (excluding biosequences).

[17] *Cf. e.g.* the classic paper of R. K. Merton: 'Priorities in Scientific Discovery: A Chapter in the Sociology of Science', *American Sociological Review*, 22 (1957), 635-659.

instead of some hundred spectacular ‘discoveries’. In addition, priority claims to new substances also play a central role for patent systems, and thus need a sound basis for juridical issues. In order to avoid priority struggles and parallel research you need a powerful classification system that meets certain requirements. Not only should it clearly distinguish between all known species according to established criteria of species identity, it should also be able to incorporate indefinitely many new species. Moreover, it should make it easy to check whether a certain species is a new one or already known.

The situation was particularly bad in the mid twentieth century. The two world wars as well as nationalistic trends split the scientific publication and documentation systems. Moreover, the number of chemical substances grew from about 100,000 in 1900 to nearly 1 million in 1950, about 95 % being organic compounds. The main reference handbook of organic chemistry, the *Beilstein*, did not come up to the needs of chemists. The literature prior to 1929 was not covered before the last issue of the second supplement to the fourth edition appeared in 1956, which, incidentally, did not distinguish between stereoisomers. And covering the literature of the period 1950-1959 was not even completed before 1987. Of the 1 million organic substances produced before 1959 and covered by *Beilstein’s Centennial Index* of 1992, we find hardly any spectroscopic characterization. Instead, the identity is determined roughly by the insufficient canonical characterization, including constitutional or configurational information if available. Checking if a certain substance has already been covered by *Beilstein* is a very ponderous procedure and requires sophisticated or even implicit knowledge in many cases. Moreover, such a check was obviously not considered to be reliable by chemists, since they continued to ‘prove’ identity with authentic substances by mixing the samples until the 1960s (Sect. 2.2).

In the early 1960s, *Chemical Abstracts* recognized the increased needs of chemists for a better system that enables quick and reliable ‘identity checks’. They “developed an algorithm for generating a unique, unambiguous machine-language representation of the two-dimensional structure of a chemical compound, together with a method for recording additional data, such as stereochemistry. This algorithm became the foundation of the CAS Chemical Registry, a computer-based system that automatically identifies structural diagrams and assigns to each a unique CAS Registry Number.”[18] Established in 1965, the registry system soon became the definite reference source for checking and claiming substance identity.

The *Beilstein* and the CAS system followed completely different strategies of database management. Following the natural history tradition, the *Beilstein* collected as many properties as possible for each substance. That was certainly meant to help future generations of chemists, but it completely ignored the main needs of contemporary chemists. Not only were there the aforementioned problems of substance identification based on the canonical characterization. When the *Centennial Index* with 1 million substances appeared in 1992, the CAS system had already registered another 10 million substances. Since the CAS system was kept up-to-date, chemists could easily use the system to lay claim to the novelty of their substances. I suspect that, unlike CAS, the *Beilstein* team failed to recognize the issue of substance identification and its social significance for making novelty claims.

---

[18] Quoted from the *Chemical Abstracts Index Guide*.

3. The impact of instrumentation

Classical chemical structure theory was largely based on chemical properties. From a logical point of view, chemical properties differ from physical properties in that they establish relations between chemical substances, between reaction partners and reaction products connected by chemical transformations. Systematically arranging all chemical knowledge yields a network structure in which every substance is related to every other substance by direct or indirect links. In such a network, the identity of each substance corresponds to its network location defined by its characteristic relations to other substances. As I have argued elsewhere, classical chemical structure theory reproduces that network on a theoretical and sophisticated level, such that the relations between substances correspond to relations between chemical structures.[19] If the identities of chemical substances are defined by relations with each other, as in the classical approach, then chemical substances are relational entities.

Spectroscopic methods, on the other hand, provide physical properties, mainly electromagnetic properties, on various sophisticated levels. The important point is that, unlike chemical properties, these physical properties do not describe relations between different chemical substances, but the response of an isolated material sample to electromagnetic fields. However small the logical difference between chemical and physical properties may appear to nonphilosophers, it became important in the second half of the twentieth century, when spectroscopic methods grew to replace the classical chemical approach of substance identification. The success story of instrumentation in chemistry, to which we turn now, is also a success story of physical properties, in the course of which the concept of species identity was modified and adapted to physical properties. At the preliminary end of that story, *i.e.* at present, not only the concept of species identity but also the kind of species are changed, from chemical substances to quasi-molecular species.

In order to analyze this process in detail and on a sound empirical basis another historiographic method is required.

3.1 A preliminary note on historiographic method

As compared to earlier periods, not only chemists but also historians of twentieth century chemistry are strongly challenged by the enormous amount of scientific work produced in the past 100 years. To give you an estimate of what has happened in quantitative terms during that period, nearly everything is now a hundred times larger than in 1900. For instance, we have now a hundred times more chemists, chemical papers, chemical substances, etc. than at the beginning of the century.[20] If you pick out a single development from the total growth, nearly everything can easily be presented as a 'scientific revolution' in one or the other inflationary meaning of that term, despite the fact that most developments show a steady annual growth rate of about 5-6 %. Moreover, historians of science need to refer to primary sources that are expected to be in some sense representative of the subject under study. Against the background of some 3 million chemists and more than 700,000 chemical publications a year today, every selection is running the risk of being arbitrary. Today we have no Boyle, Lavoisier, Berzelius, or Liebig whose opinion about chemistry might count as representative. For basic reasons, there is definitely no

---

[19] *Cf.* Schummer 1998.

[20] *Cf.* Schummer 1997a.

chemist with an overview of about more than 10 % of his field, the average overview being less than 1 %.[21] Therefore, historians of twentieth century chemistry are urged to focus on particular events, small circles, or extremely narrow scientific topics, if they wish to apply traditional historiographic methods in a serious manner.

For the topic of the present paper, standard historiographic methods are unsuitable. To understand how the development of instrumentation has affected the ontological attitudes of ordinary chemists, it does not suffice to refer to some selected writings. Even if there were an explicit discourse among a handful of chemists about such things, which is actually not the case, these opinions could hardly count as representative. In order to understand the attitudes of ordinary chemists, the millions of working chemists, we have to make a *random* selection in the statistical sense. The advantage of statistical methods is that we can clearly indicate in what sense the results are representative, including an error estimate. All we need to do is 1) to develop reasonable categories; 2) make a random selection of chemical papers of a given type; and 3) perform a document analysis of the papers with the help of the categories. In a former study, that method has even proved useful for the analysis of such difficult things as the aims that chemists are following in their research.[22]

For the purpose of the present paper, I analyzed in the above-mentioned way hundreds of randomly selected papers published in *Liebigs Annalen der Chemie* during the past 150 years. The only preselection criteria were that the papers should be from different authors/research groups and should belong to the field of synthetic organic chemistry; *i.e.* preparation and characterization of new substances should be a central part. Among chemistry journals, *Liebigs Annalen* has traditionally a high standing in synthetic organic chemistry, and a reputation for keeping strict and conservative standards in the presentation of results. Until recently, authors were mainly from Germany and some other European countries, usually belonging to an ‘elite’ with instrumentally well-equipped laboratories. As for the categories, I mainly registered what properties and what instrumental methods were used to characterize the new substances.

3.2 The rise of spectroscopic characterization since 1950

It is now well-known that spectroscopic methods caused deep changes in the subdiscipline called ‘analytical chemistry’ around 1950.[23] As one might expect, the corresponding impact on synthetic chemistry had some delay. Before 1950, chemists followed the canonical form (Sect. 2.2) in such a monotonous way that I can simply omit the quantitative results. Only after 1950, a tremendous change began that has not yet finished today. The top line in Fig. 1 provides a first rough idea of what has happened during the past 50 years. The number of spectroscopic methods (including x-ray diffraction) used on the average for the characterization of new organic compounds rose from nearly zero in 1950 to 4.5 in 2000, with the fastest growth in the 1960s.

---

[21] *Cf.* J. Schummer: ‘Coping with the Growth of Chemical Knowledge: Challenges for Chemistry Documentation, Education, and Working Chemists’, *Educación Química*, 10 (1999), 92-101.

[22] J. Schummer ‘Scientometric Studies on Chemistry II: Aims and Methods of Producing New Chemical Substances’, *Scientometrics*, 39 (1997b), 125-140.

[23] *Cf.* J.K. Tayler, ‘The Impact of Instrumentation on Analytical Chemistry’, in: *The History and Preservation of Chemical Instrumentation*, eds. J.T. Stock, M.V. Orna, Dordrecht, Reidel, 1986, pp. 1-10; and in much more detail D. Baird: ‘Analytical Chemistry and the Big Scientific Instrumentation’, *Annals of Science*, 50 (1993), 267-290.

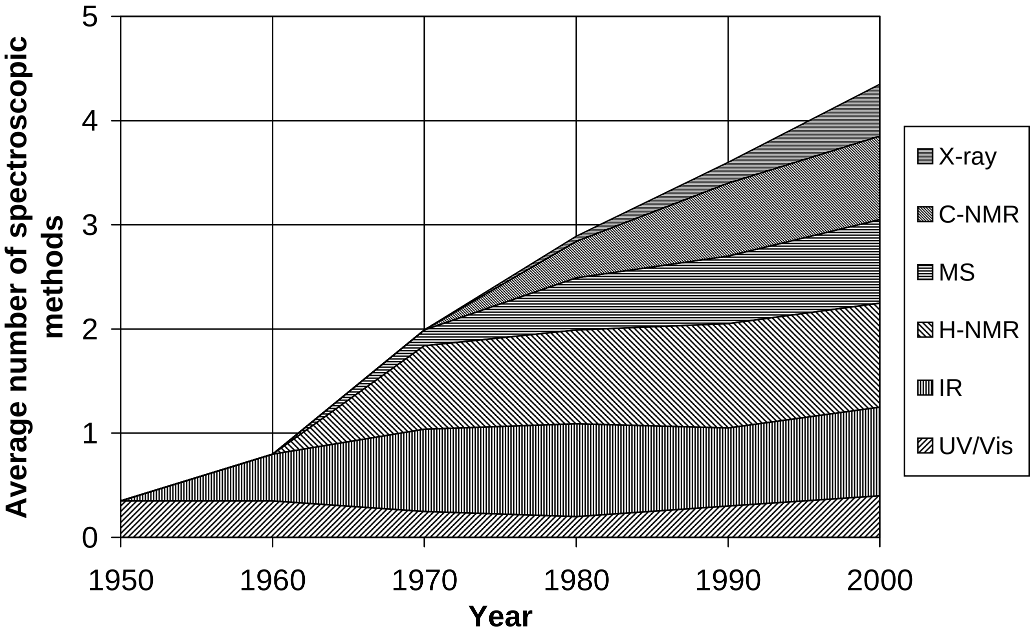

Figure 1: Average number of spectroscopic methods (including x-ray diffraction)[24] used for the characterization of new solid organic compounds in (full) papers of *Liebigs Annalen* (2000: *European Journal of Organic Chemistry*). Random selection of 20 papers at the beginning of each decade (for each method $\varepsilon \leq 11\text{-}18\ \%$, $\alpha=0.1$). Note that the 'thickness' of each layer represents the relative frequency of each method; a 'thickness' of 1.0 means that 100 % of the papers apply the corresponding method.

In 1950, the only spectroscopic method used to some extent (about 35 %) was visible and ultraviolet absorption spectroscopy (UV/Vis), available since about 1940[25]. Interestingly, this method has never become a standard procedure, but was used in the following decades only for some 30 % of substances whose color (dyes) or electronic structure attracted some interest among chemists. Not so for all the other methods presented in Fig. 1. IR spectroscopy (available since about 1943) and even more H-NMR spectroscopy (available since about 1962) rapidly grew to standard methods and remain so until today. Already in 1970, some 80 % of all new organic substances were characterized by both IR and H-NMR data. Since then, the much more expensive methods of mass spectroscopy (available for qualitative organic analysis since the late 1950s[26]) and C-NMR[27] have been steadily

---

[24] It is probably interesting to note that these are the only instrumental methods used in organic chemistry for substance characterization that have played a role worth mentioning (> 10%). For instance, given the complementary character of information from IR and Raman spectroscopy, it is surprising to find nothing of the latter. Organic chemists' confinement to a few standard techniques does obviously not depend only on the cost of instrumental equipment. Just compare the cost of, say, a 400 MHz H-NMR spectrometer with the relatively simple technology needed for measuring circular dichroism, of which I found only two instances in the whole period. Electrochemical methods are nearly absent. Only very recently, some organic chemists have been applying cyclic voltametry (10 % found in 2000). For the role of chromatographic characterization, see below.

[25] Here and in the following I refer to the "on-stream dates for several analytical techniques" collected in Tayler 1986, p. 8.

[26] According to *A History of Analytical Chemistry*, eds. H.A. Laitinen, G.W. Ewing, American Chemical Society, 1977, p. 220. Unfortunately, the book is not very reliable, mainly because it remains unclear whether the authors are telling only a US story or not.

growing to about 80 % today. The most recent trend in organic chemistry is the use of x-ray diffraction for crystallographic analysis of new compounds, which is applied to some 50 % today. We will come back to this strikingly late adoption of crystal analysis by organic chemists as compared to inorganic chemistry (single crystal diffraction goes back to 1912, powder diffraction to 1918).

Of course, Fig. 1 presents only rough trends in terms of the application of general methods. During the decades, every method has been considerably sophisticated, which is well reflected in the presentation of spectroscopic data. For instance, NMR data, while being confined to a few chemical shift data in 1970, are presented today as extensive listings of shift data and spin-spin coupling constants, occasionally combined with double-resonance technique. The main refinements of IR spectroscopy, Fourier transform technique and the application of laser (pulses), improved both precision and short-term applicability. The establishment of high-resolution mass spectroscopy caused an extraordinary proliferation of data, from a single peak, the molecular weight, in the 1970s to long series of decomposition peaks today. All spectroscopic data are presented now as listings or tables of values, usually in the 'Experimental' section that has grown correspondingly, while the more informative spectrographic plots had only a short career in the 1970s.

Today, the number of spectroscopic data determined for each new compound has grown to such an amount, that chemistry journals have been forced to put strong restrictions, in particular on crystallographic data. The 1995 'Instructions for Authors' of *Liebigs Annalen* has it that "X-ray structural analyses will only be accepted if they contribute to the solution of a chemical problem and if the crystallographic features are unique." Even then, "The structural description should be restricted to selected significant parameters." Additional data are to be deposited at the Fachinformationszentrum (FIZ) Karlsruhe, for possible later requests by individuals. More recently, some authors refer to private WWW pages where interested readers may find more data. Since chemistry journals are running a parallel internet version, they allow authors to deposit additional data on the journal's website. However, it is far from clear whether this policy meets the needs of readers rather than the needs of authors. In any case, there is a tremendous push from the authors' side to produce as many data of their new substances as possible.

3.3 Parallel changes

In parallel to the rise of spectroscopic methods, some other changes in the characterization of new substances have occurred. The short career of the refraction index of liquids is quite interesting, because that was the only conventional optical property (in a rudimentary form already measured for several liquids by Ptolemaios in the second century). At the height in 1960, soon after it became established at all, more than 60 % of organic chemists found it necessary to report the refraction index of their liquids. After then, the interest dropped steadily down to less than 10 % today. In addition, most properties of the classical canonical characterization (Sect. 2.2) received a considerable loss of interest. As one might expect, the visual characterization of crystal form does not play much of a role today (about 30 % in 2000 as compared to 90 % in 1950), whereas color – or to be more correct, the absence of color – is still reported by some 60 %. Today, chemists typically use phrases such as "a white solid" (not "white crystals") or "a colorless oil", which

---

[27] Unfortunately, I could not find any sources about when instruments for C-NMR spectroscopy became commercially available. However, since the method does not make much sense below 50 MHz (based on ^{13}C), that was probably not before the late 1960s.

means nothing else than successful purification. Reports about exemplary reactivities and solubilities have become rare or came only as implicit information, given for instance by the solvent used for recrystallization/chromatography or by further synthetic steps.

Melting points are still used for the characterization of solids (80 %), whereas boiling points for liquids have dropped down to less than 20 %. It is sometimes even impossible to recognize whether the new substance is a liquid or a solid! The reason behind that is a fundamental change in purification methods in organic chemistry. Since about 1970, chromatography has become a serious alternative for both liquids and solids. Today, about 80 % of the liquids and more than 60 % of the solids receive their final purification by one or the other chromatographic technique. Nonetheless, only few chemists use chromatographic retention values to characterize their liquids (about 20 % today) or solids (<10 %), probably because of low reproducibility and precision.

Of the classical canonical characterization, only the detailed (but now much more condensed) description of the preparation procedure and the results of the elemental analysis remained nearly unchanged. However, elemental analysis seems to have lost its meaning of providing a characteristic chemical property. As the 1995 'Instruction for Authors' of *Liebigs Annalen* suggests, it is only for proving sample purity, and as such for qualifying spectroscopic data: "The *purity* of all new compounds must be verified by elemental analysis." (Emphasis in the original.)

3.4 Towards spectroscopic substance identity

Let us turn now to the central question of how the instrumental development has affected the concept of chemical species identity. The way chemists have implicitly dealt with that issue suggests three more or less successive approaches. The first two are adaptive strategies; the third one, in some sense a consequence of the second one, has lead to a fundamental ontological change.

3.4.1 The fingerprint approach

At the earliest stage, until the early 1970s, the canonical characterization of new compounds remained relatively robust. Spectroscopic data, in particular IR data, were considered as additional characteristic features of new compounds.[28] First of all, spectroscopic data are simply a series of optical material properties, *i.e.* absorption coefficients at different wavelength. Given a certain precision, spectrographic plots provide sufficiently rich information to distinguish between millions of pure substances. More than any property of the canonical characterization, including the refraction index that was temporarily established for that purpose, such a plot meets the requirement for determining substance identity in an unambiguous way – it provides a '*fingerprint*', as chemists began to call it.

Such fingerprints, or the reduced form of a set of characteristic peak data, were soon applied to substance identification. Instead of determining mixed melting points with 'authentic samples', some chemists began to prove identity by comparing the spectra. The first obstacle was of course the lack of spectra of known substances. When a considerable number of spectra were recorded, the next problem was how to match a new spectrum with thousands of spectra of the library. As early as the 1950s, before the rise of comput-

---

[28] Note that the present analysis is based on research papers reflecting the average view of working chemists, whereas some prominent individuals including textbook authors already had rather 'futuristic' views in the same period.

ers, a mechanical device was already constructed for that purpose.[29] For each substance, the characteristic IR data were coded by punched holes on a paper card. The complete set of cards were then machine-sorted, such that two cards with same holes could automatically be identified. However, the mechanical device never found its way to the standard equipment of chemical laboratories.

It is well known that the fingerprint approach experienced an extraordinary revival since the digitalization of spectrometers. Today's standard spectrometers of all sorts are now routinely equipped with computer databases ('libraries') that allow 'fingerprint identification' while recording the spectra.

3.4.2 The structure determination approach

We saw already that the classical way to overcome the insufficiency of the canonical characterization was by chemical structure determination. The identity of a chemical substance was fixed by collecting as many chemical properties as needed for an unambiguous structural interpretation. This was largely accomplished by assigning 'functional groups' to a 'carbon skeleton' according to certain chemical properties. Very soon, chemists realized that both IR and NMR spectroscopic data provide useful clues for that purpose. The fast establishment of these two methods, as compared for instance to UV/Vis spectroscopy,[30] was because they provide characteristic signals for many 'functional groups'.

However, there was anything else than a sudden replacement of the original chemical method. On the contrary, the method of structure determination remained basically the same from a logical point of view, *i.e.* chemical and spectroscopic properties were both used in the same way. If the carbon skeleton and the kinds of functional groups attached are determined, there are frequently still a lot of different constitution formulas possible. A typical procedure of structure determination goes by step-wise exclusion of possibilities, until a single possibility is remaining. Chemist use all sorts of arguments, be it from chemical or spectroscopic properties,[31] to exclude structural possibilities, as long as the arguments are sound in some sense. Thus, spectroscopic properties could be easily incorporated into the chemical approach of structure determination and thus substance identification.

On a closer look at the way chemists have been arguing for their structures, the role of spectroscopic data for structure determination has gradually changed together with the kind of structure to be determined. Surprisingly, only as late as 1960 all new substances were characterized by *constitution* formulas. With the exception of few special cases (*e.g.* sugars), *configuration* formulas became the standard form only in the late 1980s. And it is only in the past couple of years, that *conformation* structures play a considerable role (> 10 %), mainly in combination with crystallographic analysis by x-ray diffraction.

The typical way chemists used spectroscopic data in constitution analysis until the 1980s is by confirmation. After the constitution is determined by means of traditional chemical methods, they argued that the result is confirmed by analogy with spectra of known (structurally determined) compounds. At least that is how they explicitly argued in the main part of their papers. In addition, it very early became a standard presentation

---

[29] *A History of Analytical Chemistry*, p. 158.

[30] Since the 1980s, UV/Vis spectroscopic characterization has been increasing again (Fig. 1) because the method can conveniently be used in-line with HPLC (high pressure liquid chromatography).

[31] I should add that chemists occasionally include also quantum chemical calculations in their argumentation and thus completely ignore what philosophers have taught about the difference between theory and experiment.

in the so-called 'Experimental' part to give spectroscopic data in an interpreted form, *i.e.* to every IR peak is assigned a bonding or functional group, to every H-NMR peak a proton. That suggests that confirmation was achieved rather by a complete structural interpretation of the spectra than by mere analogy. When configuration entered in the late 1980s, the kind of explicit argumentation changed. I assume that constitution was still determined in the traditional way, mainly by following reaction steps on the constitutional level by well defined reaction mechanisms. There are still a few cases until today (mainly in natural products chemistry), where authors explicitly claim to have determined the (relative) configuration by purely chemical means. However, the typical argument for a certain configuration gradually became that it is "proved" by spectroscopic analysis (mainly by NMR).

In other words, spectroscopic methods gradually received more weight in structure determination along with the shift from constitutional to configurational analysis. Contrary to what many might have expected, it is only in the past 10-15 years that spectroscopy has become accepted by ordinary chemists as an *independent* standard means for the determination of the structure of a new substance, and as such also for determining substance identity.

3.5 From substance identity to molecular species identity

The finger print approach as well as the structure determination approach, both in its classical chemical and spectroscopic form, are means to determine chemical substance identity. From a logical point of view, molecular structure, as the outcome of a sophisticated theoretical interpretation of chemical and spectroscopic properties, is a complex theoretical property of material samples and, consequently, of a chemical substance. Insofar as molecular structure serves to determine substance identity, we may consider it an outstanding (but not the only!) essential property of chemical substances. It is important to stress the ontological status: a molecular structure is a *property* of a chemical substance. Speaking in general philosophical terms, substances are ontologically prior to properties – no property without a substance.

The final point I would like to make is that spectroscopic instrumentation has radically undermined this ontological status. During the past decades, chemists' ontological attitude has seriously changed, comparably only to the turn from the metaphysical to experimental concepts of species identity in late eighteenth century chemistry. Molecular structures are no longer considered *properties* of substances; they are now the species whose identity is to be determined and which are subject to chemical classification. In this attitude, talking about material substances seems to have become obsolete.[32]

Of course, there was always a metaphysical tradition preferring to speak of geometrical structures instead of material substances, which goes back to Plato's *Timaios*. However, the majority of chemists basically remained antimetaphysical since the late eighteenth century. The lack of interest in, sometimes even the antipathy against, philosophy let them use concepts such as molecular structure in a pragmatic way, as conceptual tools for their purposes without caring much about ontological implications.[33] Moreover, until today there is a certain kind of ambiguity in ordinary chemical language that conceals the

---

[32] *Cf.* also P. Laszlo, 'Chemical Analysis as Dematerialization', *HYLE–International Journal for Philosophy of Chemistry*, 4 (1998), 29-38.

[33] *Cf. e.g.*, P.J. Ramberg: 'Pragmatism, Belief, and Reduction. Stereoformulas and Atomic Models in Early Stereochemistry', *HYLE–International Journal for Philosophy of Chemistry*, 6 (2000), 35-61.

ontological issue at stake.[34] Chemists typically use the same terms and names to refer to both material substances and molecular structures. Sometimes they drive the ambiguity to extremes. For instance, after defining a symbol '**11a**' for a suggested configurational structure in the main part of a chemical paper, the authors tell us in the experimental section that they have put 6 g of **11a** in a vessel and then cooked for 2 hours!

What evidence do we have then for an ontological change? And why should spectroscopic methods have had any impact on that? The first indirect clue is the parallel decline of the canonical substance characterization. Today, *material* characterization of new products is reduced to the utmost minimum for making the preparation reproducible; sometimes even that appears to be a problem if, for instance, no data (boiling point or retention value) of the corresponding purification fraction is provided. On the one hand, due to the sophisticated instrumentation, spectroscopic characterization has become possible at a micro-level where classical methods of substance characterization fail. On the other hand, if spectroscopic analysis is directly coupled with chromatographic separation, one can determine molecular structures in-line, so to speak, without any intermediary step of material characterization. Molecular structures have no boiling points, melting points, and colors, as chemical substances do. If the former have become the objects of chemical investigation and classification, there is definitely no need for such data.

Another indirect clue is the most recent interest in structure analysis by x-ray diffraction. Contrary to most spectroscopic methods, x-ray diffraction does not fit the traditional chemical method of structure determination but is rather a completely independent method that provides structures of quite a different type.[35] Conformational analysis, as one of the major purpose of x-ray diffraction today, was formerly of less interest, since one could rarely put different conformational forms in different bottles, let alone reaction vessels. Two conformational forms were considered to belong to the same chemical substance. Thus, even the relatively liberal *Chemical Abstracts* – in a sense, the professional guides in ontological issues – did not register different conformational forms until at least 1996.[36] The recent interest in conformational analysis suggests a change of perspective, however, such that structural differences at the conformational level of the same substance become constitutive for making a distinction between different species.

There are even more direct proofs of an ontological change or crisis. Spectroscopic methods frequently allow determining molecular structures of mixtures. Hence, the object under empirical investigation need not be a pure chemical substance. That is to say, you can spectroscopically determine the identity of a molecular structure without having a corresponding chemical substance. Since spectroscopic analysis of mixtures is sometimes subject to failure, chemistry journals usually demand purification including purification tests by elemental analysis (Sect. 3.3). However, there are cases where purification is impossible, simply because a chemical substance corresponding to the molecular structure cannot exist.

---

[34] In a recent paper, Emily R. Grosholz and Roald Hoffmann have argued for the productivity of such ambiguities in the forefront of research ('How Symbolic and Iconic Languages Bridge the Two Worlds of the Chemist: A Case Study From Contemporary Bioorganic Chemistry', in: *Of Minds and Molecules*, eds. N. Bushan, St. Rosenfeld, New York, Oxford University Press, 2000, pp. 230-247).

[35] *Cf.* Schummer 1998, p. 149-151.

[36] *Cf. Registration Policy for the CAS Chemical Registry System*, Columbus, OH, p. 6; I refer to the version valid at least until 1996, which was not changed over the past 30 years (personal communication).

There are three main examples of that kind. The first one is the so-called 'matrix isolation spectroscopy'.[37] A gaseous reaction mixture is mixed with gases like argon and then rapidly frozen up such that intermediary states, which cannot be isolated by purification, are trapped in the solid argon matrix that is then subject to various spectroscopic investigations. The second one is high-resolution mass spectroscopy providing a series of mass peaks that can be interpreted as signals of certain molecular fragment species. The third example is the application of high-speed spectroscopy, usually promoted as 'femto second spectroscopy', which uses short laser pulses and Fourier transform analysis of the responses. That method enables the determination of molecular structures of intermediates and so-called van-der-Waals complexes,[38] either in solutions or in molecular beam collision experiments, with life times in the range of 10^{-13} s.

All these methods provide data for structural characterization of molecular or quasi-molecular species, for which we have no corresponding chemical substances.[39] Thus, structure determination no longer serves to determine substance identity alone. Instead, it has become an independent means for determining identity of a new kind of chemical species, molecular or quasi-molecular structures. Once spectroscopic methods were established as an independent means for structure determination, a fundamental ontological change in chemistry started.

Chemists know well that *Liebigs Annalen* was one of the most conservative journals in that it stubbornly rejected papers about these new species, whereas most other journals, even the parallel German *Chemische Berichte*, were much more liberal already in the late 1980s. Only after *Liebigs Annalen* merged with other European journals to form the new *European Journal of Organic Chemistry* in 1998, do we also find reports on the new chemical species there. Overall, the number of these quasi-molecular species reported in chemistry journals is still very low today, much less than 1 %. However, the mere fact that a few became accepted as chemical species by the chemical community, and were even assigned registry numbers by *Chemical Abstracts*, proves that the fundamental ontological change has already happened. Officially, the conservative reservations of *Liebigs Annalen* were meant to avoid errors in data interpretation. They demanded elemental analysis of isolated chemical substances in order to prove purity for making spectroscopic analysis free of possible errors. However, I suspect that there were tacitly also deep reservations about the ontological change at issue.

4. Conclusion

Spectroscopic instruments are tools for various purposes. Analytical chemists use them for qualitative and quantitative analysis, *i.e.* for collecting information about what kind

---

[37] The first infrared spectroscopic analysis of 'matrix-isolated' molecular species was reported by George C. Pimentel and co-workers in 1954. For brief, more or less historical notes on that technique see W.J. Orville-Thomas: 'The History of Matrix Isolation Spectroscopy', in: *Matrix Isolation Spectroscopy*, eds. A.J. Barnes et al., Dordrecht, Reidel, 1981, pp. 1-11. Note that 'matrix-isolated' is a nonsense term, *i.e.* a *contradictio in adjectum*, since the molecular species are not isolated but frozen up in a solid *solution*. Using the term 'isolation' was probably part of rhetoric to make the new approach acceptable by conservative chemists.

[38] *Cf.* also J.E. Earley: 'Modes of Chemical Becoming', *HYLE–International Journal for Philosophy of Chemistry*, 4 (1998), 105-115.

[39] Interestingly, the CA Index Guide of 1996 still says, "Intermediates that are not isolated and characterized are not indexed". A brief look into a 1990 volume of *Chemische Berichte* reveals, however, that also 'non-isolated' molecular species, *e.g.* carbocations, received CAS registry numbers if they were spectroscopically characterized. To be sure, the rhetorical use of 'matrix isolation' has helped here.

and how much of an already known species is present in a given sample. In addition, spectroscopic instruments are used today for the first characterization of new species, on which analytical chemistry depends. Species characterization intends to fix the identity of a species by providing sufficiently many properties considered as essential properties. Thereby, a concept of species identity is presupposed which is the topic of the present paper.

We have seen that classical modern chemistry dropped both metaphysical principles and merely observational properties and considered experimental properties, mainly chemical properties, as essential for determining the identity of pure chemical substances that were thereby considered the basic species of chemistry. Since that concept of species identity drew on an open and potentially infinite set of essential properties, practical substance identification by comparing properties of samples was necessarily provisional and vague. Classical chemical structure theory provided a solution to this problem by selecting those chemical properties as essential properties which are sufficient for chemical structures elucidation. This means that chemical structure, as a complex theoretical property of a chemical substance, is its essential property. However, due to the hypothetical character of chemical structure elucidation, many chemists remained reluctant to base substance identification on structural identity alone. Instead, in all crucial cases, chemists avoided both the vagueness of the empirical approach and the hypotheticity of the theoretical approach and relied on an operational concept of species identity by mixing samples and investigating mixing effects. Such was the situation in the mid twentieth century, before spectroscopic instruments moved into the chemical laboratories.

At first, spectroscopic methods supplemented and improved traditional approaches of determining substance identity. As to the empirical approach, spectroscopic plots or data sets provided sufficiently rich information to be used as characteristic fingerprints of millions of substances, and thus replaced the operational approach even in crucial cases. As to the theoretical approach, particularly IR, NMR, and MS data provided specific information to be used in chemical structure elucidation, and thus put chemical structures on a more secure basis than before. In the course of instrumental refinement, spectroscopic methods slowly became acknowledged as *independent* and reliable standard means for structure elucidation on both the constitutional and configurational level in the 1980s, which caused a change of the ontological attitude of chemist in two steps.

Originally, the basic species of chemistry were chemical substances whose identity were determined first by experimental properties and then by molecular structures as complex theoretical properties. In classical chemical structure theory, molecular structures were hypothetical entities whose ontological status each depended on the hypothesis of structure elucidation of the corresponding substance. The more structure elucidation was supplemented by spectroscopic means on independent grounds, the more did chemists conceive of molecular structures as real entities.[40] Thus, chemists no longer considered molecular structures simply as properties of chemical substances; instead, molecular species became ontologically on par with chemical substances. The doubling of chemical species was not reflected by chemists as they used the same terms and names for both kinds; nor had it an impact at first on the practice of species identification, since classical chemical structure theory presupposed as its basic theorem a strict one-to-one relationship between chemical substances and molecular structures (at the configurational level).

---

[40] See also L. Slater: 'Organic Chemistry and Instrumentation: R. B. Woodward and the Reification of Chemical Structures' (in this volume).

Nonetheless, there were two different kinds of species waiting for a decision on which should count as the basic one in chemical classification.

The most important impact of spectroscopic methods was that it finally made chemists decide in favor of molecular species. Once established as independent means of structure determination, spectroscopic methods were also used to characterize quasi-molecular species for which there exist neither a corresponding chemical substance nor a classical approach of chemical structure elucidation, such as conformational states, intermediary states in solution, van-der-Waals complexes, molecular fragments in MS. The fact that chemists, since a couple of years only, consider these quasi-molecular species on par with common molecular species proves that they have dropped chemical substances as the basic chemical species.

Such a decision has many far-reaching consequences. One the one hand, chemical classification becomes much more complex and allows deriving more differentiated concepts than before. On the other hand, the change also implies many new ontological and conceptual problems that most chemists are probably not aware of.[41] Species defined by spectroscopic properties alone, *i.e.* by physical properties, are no longer relational entities as chemical substances and classical structural formulas are and, thus, loose chemical information about reactivities. Furthermore, there is a lack of well-defined identity criteria for the new quasi-molecular species due to the ambiguity of the term 'molecular structure'.[42] For instance, shall we consider all possible conformations or all rotational states as different chemical species? How many quasi-molecular species shall we allow in pure water? Shall we really consider again a change of aggregation state as a change of species identity? Without reasonably selected criteria for species identity of quasi-molecular structures, chemical species classification will definitely collapse. Spectroscopic instrumentation does not provide such criteria. It is simply a tool that is going to challenge chemists to reflect on their ontological attitudes.

Acknowledgement

At the earliest state of this paper, my brother, organic chemist Dietmar Schummer, helped me to clarify possible misunderstandings. I am grateful also for the many useful comments I received from historians of chemistry at the conference, particularly from the official commentators Arnold Thackray and James Bennett. The final version greatly benefited from detailed and extremely helpful comments from both chemists and philosophers: Giuseppe Del Re, Joseph E. Earley, Robin F. Hendry, Roald Hoffmann, Jaap van Brakel, Stephen J. Weininger and Guy Woolley.

---

[41] For more details on these conceptual and ontological problems see Schummer 1998, pp. 139-43. A rare exception among chemists is R. Hoffmann, *The Same and Not the Same*, New York, Columbia University Press, 1995, part I.

[42] Here, all the arguments against microstructural essentialism apply, see J. van Brakel: 'Chemistry', in: *Handbook of Metaphysics and Ontology*, eds. H. Burkhardt, B. Smith, München, Philosophia, 1991, vol. I, pp. 146-147.