Special Review

HISTORICAL DEVELOPMENT OF THERMOANALYTICAL METHODS

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Thermal tests in antiquity and in the Middle Ages. Blowpipe tests. Measuring temperature and the development of thermometers. Latent heat. The nature of heat. Amount of heat. Differential thermal analysis. Differential scanning calorimetry. Heat treatment of precipitates. Thermobalances. Thermoanalytical methods associated with determination of evolved gas. Thermometry, enthalpimetry.

The spectacular development, in recent decades, of thermoanalytical methods all over the world might easily make one think that these methods represent an entirely novel direction in analysis.

Actually, whatever hypermodern instruments are at present being used for thermal analysis, thermal procedures were the oldest methods of analysis, though not termed, at that time, thermal analysis, but fire methods of the art of assaying.

Fire tests

Civilization started with the power of man over fire. Fire was applied to produce objects for general use, metals were obtained from ores by means of fire, and fire was used to produce tools from metals. No wonder, recognizing this significance of fire, that old myths describe the acquisition of fire as a miracle: men, as it were, stole fire from the Gods.

For a long time chemistry was an art of fire, and only relatively recently became an art of solutions. Alchemists scantly applied dissolving their major operations were melting and distillation and their most important piece of equipment the oven. In fact, there were many substances which they were incapable of dissolving, since mineral acids were invented only in the late Middle Ages. To produce them by the dry distillation of their salts also necessitated the power of fire.

It is therefore small wonder that "thermal" methods of analysis preceded chemical methods. In the course of time most of these old thermal methods were superseded in practice by more modern techniques.

This statement is, however, not valid for the most ancient thermal method, namely for cupellation to assay gold: this is in use up to the present for official tests. The first references to this method are found in the Old Testament, for instance in the Book of Zechariah: "Then I will pass this third through the fire and I will refine them as silver is refined, and assay them as gold is assayed" [1]. Other references can be read in the Books of Ezekiel and Isaiah [2]. A Greek author, Agatarchides (2nd century B. C.) described the process in more detail [3]. Numerous documents and detailed instructions how to carry out this gold assay have remained from the Middle Ages, among others in decrees of King Charles I of Hungary (1342) and King Philip VI of France (1343).

The various so-called cementation methods, dating back to antiquity and the Middle Ages, for the separation of gold from silver were also fire methods. These procedures, ofthen rather obscure and complicated, were carried out in the melt. The first written instruction is found in the work of Plinius [4].

Further "thermal" tests from antiquity are described in the Leiden Papyrus from ancient Egypt. Gold was tested by ignition: if it remained unchanged, it was pure, if it became harder, it contained copper, if it became whiter, it contained silver. Tin was tested for purity by heating to the melt and pouring it on a sheet of papyrus. If the papyrus was reduced to ashes, the metal was pure. If the metal contained lead, the papyrus sheet did not burn (evidently, because the alloy melts at a lower temperature than the pure metal) [5].

The thermal method to which science is indebted most of all, the method that led to the vast development of chemistry in the 18th century, to the discovery of many new metals made use of a very simple device, a little tube by means of which air could be blown into a flame. The sharp, high-temperature flame obtained was directed to the ore placed in a cavity of a piece of charcoal. The result of the reduction process taking place was a metal bead called "the king". The small device was the blowpipe, the indispensable instrument of qualitative analysis up to the end of the 19th century, when it was successively substituted by spectroscopy.

The blowpipe came from the glass manufacture. The first indications of its potentials for analysis are to be read in Kunckel's "Ars vitraria experimentalis" (1689) [6]. In the following 150 years numerous books appeared dealing with the use of this simple and greatly useful device. Analysts of that period like Cronstedt, Rinmann, Bergmann, Marggraf, Gahn, Berzelius understood to use the blowpipe with the skill of a conjurer.

By means of various salts as additives (cobalt, borax etc.) more and more specific methods of detection were developed.

Johann Heinrich Pott carried out systematic studies concerning the thermal behaviour of various substances. His objective was entirely practical: commissioned by the King of Prussia, he attempted to determine the composition of Meissen porcelain, at that time a strictly guarded secret of the King of Saxonia. He hoped to reach his goal by studying the behaviour of various minerals and their mixtures with salts in fire at different temperatures. He noted all phenomena observed (melting, change of colour, etc.). Though he did not succeed in solving the composition of porcelain, the results of his several thousands of experiments published in 1746 furnished valuable data to chemists [7].

Temperature

The greatest problem in these old methods was the reproducible recording of temperature. For a long time temperature could only be sensed, but not measured. Thermometers are inventions of modern times.

The pioneer in temperature measurement was Galilei. He used a glass tube sealed with water, immersed into a vessel filled with water. Thermal expansion and contraction of the air, that is, the height of the water column indicated temperature changes.

The scientists of Galilei's school, the members of the "Accademia del Cimento" Florence – which was the archetype of the academies of science in modern times – intensely studied temperature measurement around 1660. They turned from air to various liquids (alcohol, mercury) and profited from their readier observable volume changes with temperature. They sealed the tube, in order to eliminate the effect of atmospheric pressure. They also employed certain graduations on their spiral capillaries, which were true masterpieces of the art of glass-making, to facilitate following of volume changes. Subsequently, fixed points were used for graduation. These fixed points largely differed: they included the temperature of the human body, the temperature of a certain cave or source, the melting temperature of butter, etc. By means of these graduations they found out that state transformations, e.g. freezing and boiling of water always appear at the same temperature. Among various proposals for fixed points, that of the German scientist Fahrenheit (1724) became widely accepted. His two basic points were the freezing point of a mixture consisting of ice, common salt and ammonia, and the temperature of the human body. He divided the distance between these points into 96 degrees [8]. The freezing point of water on this scale is 32 °F, the boiling point of water 212 °F. Réaumur's scale (1730) spread above all in his own country, in France. His fixed points were the freezing point and boiling point of water, and he divided the distance into 80 degrees, because the liquid used in his thermometer, a mixture of water and alcohol, expanded by the 80th part of its initial volume over this temperature range [9]. The Swedish scientist Celsius used the same fixed points, but divided the distance into 100 degrees, with 0 for the freezing point and 100 for the boiling point of water [10]. This appears quite natural to us, but was not natural at all at the time, since neither money nor measures went by the decimal system. Only after the introduction of the metric system did the Celsius scale replace the other scales in most countries, apart from those as Great Britain and the United States who did not adopt the metric system.

Thermometers made of glass and filled with a liquid were unsuited for measuring high temperatures. Physicists soon found further means to cope with this problem. Mortimer was the first to utilize the thermal expansion of metals for temperature measurement [11]. He recorded the thermal expansion of a brass rod on a semicircle scale, making use of a sophisticated transmission. The sensitivity and efficiency of metal thermometers rapidly increased with the use of bimetallic strips. Preliminary experiments were already made in the 18th century, but the merit of the invention is due to Crichton (1803) [12], and that of further improvement to the watchmaker Bréguet (1817).

Soon electrical phenomena were also utilized for temperature measurement. Seebeck observed, in 1822, that an electrical current flows in a circuit consisting of two different metals, when the temperatures of the two junctions are different [13]. Nobili made use of this phenomenon in 1830 for temperature measurement [14]. Various thermocouple designs were subsequently developed, the most successful being the Pt–PtRh thermocouple introduced by Le Chatelier at the end of the 19th century.

Already Davy discovered that the electrical resistance of metals changes with temperature [15]. However, this principle was put into practice for temperature measurement only 50 years later by William Siemens, using a platinum filament [16].

Optical pyrometers were introduced by Le Chatelier in 1892. A significant step in the field of temperature measurement was made by Sillery in 1942 with the invention of the thermistor [17].

The absolute thermodynamic temperature scale or Kelvin scale has been known in science already from the middle of the last century. However, the kelvin only became the official unit of temperature in 1969.

Heat

Measurement of heat was a later achievement than measurement of temperature. Joseph Black was the first to pay attention to the quantity of heat. He found in 1761 that melting ice and boiling water "conceals", that is, absorbs much heat without changing its temperature. He called this amount of heat "latent heat". The term is characteristic for the contemporary interpretation of heat. Within the scope of this paper we cannot go into details concerning the views of natural philosophy and physics on the nature of heat. To put it briefly: It is well-known that heat was one of the four elemental properties discerned by Aristotle. He defined fire, one of the four elements, as consisting of the elemental properties "hot" and "dry". Long after the decline of Aristotelian doctrines the material nature of heat was still not contested, although in another theory also conceived in antiquity, namely Demokritos's atomic theory, another alternative was already outlined: that of heat being motion. After the revival of the atomic theory such notions could indeed be found in the work of some scientists of the 18th century, for instance Lomonosov and Bernouilli. The majority of scientists, however, continued to believe that heat is an infinitely light, unweighable, floating liquid: heat substance. Black, e.g. assumed that free heat substance disappears when water freezes, because it combines with the atoms of ice and thereby becomes latent.

The two opinions lived side by side in peaceful coexistence, most peacefully of all in the fundamental work of Laplace and Lavoisier establishing the basis of calorimetry (1783). The two scientists constructed an ice calorimeter, in which they determined the heat of melting for ice as well as the heat of combustion and the specific heat for numerous substances. They expressed the amounts of heat by means of the mass of ice melted as the result of the respective process. In the introduction to their work the authors pointed out that their opinions concerning the nature of heat were different. Lavoisier who expelled fire substance, i.e. phlogiston from chemistry, non the less regarded heat as something material, whereas Laplace considered it as the result of the invisible motion of molecules [18].

The latter opinion then gained ground in the past century, while we now again assume a kind of duality in the nature of heat.

The marvel of the steam engine materialized in industry towards the end of the 18th century. It drove machines, it produced work. Consequently much attention was paid in the following decades to the problem how heat is turned into mechanical energy. Sadi Carnot, in his brilliant paper entitled Reflexions on the Motion Power of Fire (Réflexions sur la puissance motrice du feu) that appeared in 1824 and was disregarded for a long time, and which, among others, contains the Second Law of Thermodynamics, unequivocally stated that heat is the result of the motion of particles. Studies on the kinetics of gases and various observations in other fields subsequently led, around the middle of the past century, to the development of a new branch of physics, namely thermodynamics. The merit is due above all to Clausius, Thomson and Helmholtz. Thus the nature of heat appeared fully disclosed. However, doubts already arose in Maxwell: could heat not be a sort of radiation? Max Planck then actually classified it as radiation.

Parallelly to thermodynamics and influenced by it, thermochemistry was developed, by the work of Dulong and Petit, Hess, Favre and Silbermann. Important notions and definitions were established in the course of these studies. The unit and term calorie was introduced by Favre and Silbermann in 1853 [19]. The notions enthropy and enthalpy were devised by Clausius, the terms exothermic and endothermic by Berthelot [20].

Le Chatelier was the first, in 1887, to utilize the enthalpy changes taking place in the course of thermal treatment of substances for the determination of the composition of minerals [21]. The apparatus that he constructed for this purpose consisted of a gas oven in which he heated clay minerals. A thermocouple was embedded in the clay, and a galvanometer indicated how the change of the temperature of the substance followed heating temperature. The galvanometer lamps were switched on at equal intervals of time, and the light signal reflected by the mirror was photographically recorded. In this way, a line-hatched scale was obtained, where increased denseness of the lines indicated an exothermic process. This was, in fact, the archetype of differential thermal analysis, the latter method being developed by Roberts-Austen in 1899 [22]. Roberts-Austen used, in addition to the substance to be tested, a second substance unchanged by the thermal treatment, and measured the temperature increase in both substances with thermocouples connected in opposition. The galvanometer indicated a current only when a temperature difference arose between the two substances, i.e. when a change in the enthalpy of the substance being tested took place.

Roberts-Austen recommended his method for metallographic studies. With this method the principle of differential thermal analysis was established, only slight modifications followed: Kurnakov suggested the use of a rotating drum for photographic recording in 1904 [23], Hollings and Cobb introduced controlled atmospheres in 1915. However, the method was mainly used for metallographic, physicochemical and mineralographic studies, whereas applications in chemical analysis were scarce, probably because it supplied only qualitative information. Kracek appears to be the first who attempted quantitative evaluation of DTA results [24] followed by a wealth of literature devoted to the problem. It was the combination of DTA with other methods, above all with thermogravimetry which resulted in its introduction into analysis.

A new system – named differential scanning calorimetry (DSC) – has been reported in 1964 improving the utility of the DTA technique for quantitative analysis. The DSC system measures the differential energy required to keep both sample and reference at the same temperature throughout linear heating. Watson, O'Neill, Justin and Brenner [25] who described the method mentioned Sykes (1935) [26], Kumanin (1947) [27] and Eyraud (1954) [28] as precursors.

Weight change

Analysts were always aware of the importance of weight constancy of analytical precipitates. Until the middle of the past century inorganic reagents were used almost exclusively for precipitation. Such precipitates were able to withstand ignition to high temperatures used practically in all cases, since only flame and oven were at disposal. Drying was too elaborate; if it was unavoidable, like e.g. with silver chloride, the water bath was used, or else drying was carried out in the exsiccator over sulfuric acid or calcium chloride. Hence the temperature of the thermal treatment did not play an important part.

We found the first data on thermal testing of analytical precipitates with the aim of determining their thermal stability in Fresenius's classical "Instruction to Quantitative Analysis" (Anleitung zur quantitativen Analyse) (1847). There one reads, for instance, that calcium oxalate should be weighed in the form of calcium carbonate, since the oxalate contains one molecule of combined water which is evolved between 180 and 200 °C, and the residual oxalate evolves carbon dioxide at red heat and is converted into carbonate. At still higher temperatures the carbonate is gradually converted into the oxide, but this process is not complete even at the highest temperatures attainable. Regarding silver chloride Fresenius lists a melting point of 260 °C. Consequently, he must have carried out some sort of thermal study, but, to our regret, did not describe it.

In many books on thermal analysis Nernst and Riesenfeld are pointed out as designers of the first thermobalance. This, however, seems to be erroneus. In their often cited paper entitled Quantitative Gravimetry with Very Small Amounts of Substances [29] they only described a novel, simple torsional microbalance, with which he measured substances before and after heating, but no thermobalance. Earlier, Nernst reported on a novel oven electrically heated with platinum wire [30]. Subsequently Brill, in 1905, coupled the two instruments for a study on the dissociation of alkali earth carbonates [31]. In his apparatus a small crucible hanging on the beam of the torsion balance reached down into the electric oven. He weighed the sample during heating and recorded weight changes *versus* temperature, that is, thermogravimetric curves. His experiments were carried out in a protective gas atmosphere of dry carbon dioxide which he led into the oven through a magnesite tube. This apparatus should be regarded as the first thermobalance.

Urbain and Boulanger, in 1912, designed a thermobalance serving as zero-instrument [32].

A simple thermobalance for practice was built by Honda in 1915 utilizing the common analytical balance [33]. Further improvements and other designs of the thermobalance were suggested between the two World Wars by Guichard [34], Dubois [35] and Chevenard [36]. None the less thermogravimetry was not particularly widespread and only infrequently used in this period.

The great boom came in the 'fifties. Duval published a series of papers on the thermogravimetric study of almost one thousand analytical precipitates using the Chevenard balance [37]. The expectations that the temperature values of the thermogravimetric curves will yield reproducible characteristics of the various precipitates did not prove to be true, but none the less these curves appeared very helpful in the determination of the composition of largely differing substances, and thus the method reached great popularity.

Combined methods

To achieve better evaluation of TG curves, instruments and designs were invented for automatic recording of the derivatives of the TG curves, that is, DTG curves (De Keyser, 1953 [38], Erdey, F. Paulik and J. Paulik, 1954 [39], Lambert, 1958 [40]). The DTG curve, recorded simultaneously with the TG curve, allows an exact interpretation of the latter. Subsequently Erdey, Paulik, and Paulik designed an instrument (1955) suited for simultaneous recording of TG, DTG and DTA curves [41]. A further development of the design led to the Derivatograph, the first complex thermoanalytical instrument. Various complex thermoanalytical instruments have since been commercialized by different companies, and further thermal methods have been included like methods associated with evolved volatiles or with dimensional change.

Evolved gas detection and analysis, that is, following a thermal process by detecting or determining the nature or amount of volatile products formed in the process is a relatively young method. It developed from the DTA method. Berg was the first to measure, in 1933, the volume of the gas evolved in each step at stepwise heating [42]. In the early 'fifties the method of evolved gas analysis proper, and the apparatus involved, was developed above all by Teitelbaum and Berg [43], and Gordon and Campbell [44], resp. The first technique based on dimensional change, that is, dilatometry can, however, be led back to the 18th century. The famous porcelain manufacturer Wedgwood prepared geometrical bodies from clay, heated them to red-yellow heat, and measured their dilatation after cooling with a self-designed apparatus and expressed it in Wedgwood degrees [45]. The pioneer of modern dilatometry was Chevenard in 1917 [46].

The development of thermal analysis in recent years has been characterized above all by the combination of thermal methods proper with other analytical methods like X-ray spectroscopy, IR spectroscopy, gas chromatography, mass spectroscopy, etc. Such combinations resulted in a mutual increase of efficiency of the methods involved.

Thermometry, enthalpimetry

Somewhat arbitrarily thermometric and enthalpimetric analyses are also included in thermal methods, whereas they are in fact solution methods and thermometry should rather be classified as titrimetry. (It is called thermometric titrimetry too.)

The principal difference is that in thermoanalytical methods mentioned above some property of the system to be studied is recorded as a function of temperature, whereas in thermometry and in enthalpimetry temperature is recorded as a function of the amount of reagent added [47].

One has to distinguish the two methods more clearly as far as in thermometric titrimetry temperature change is used to endpoint detection of a reaction, whilst in enthalpimetric analysis temperature change is used as measure of the amount of the reaction product. However, at the beginning no distinction was made, even the methods have not been named as new ones.

The pioneer in this field was H. Howard [48] in 1910. He attempted to determine the concentration of sulfuric acid from the temperature change arising at dilution. The same method was developed for "The rapid estimation of the strength of sulphuric acid" by Richmond and Merreywether [49]. They made no claim to the originality of the method and what is more besides the above mentioned H. Howard also referred to a certain C. B. Howard. He may have communicated his results to the Finsbury Technical College Chemical Society in 1886, but exact details of his work could not be found as early as 1917 either.

The first thermometric titration (named temperature method) was carried out by Bell and Cowell in 1913 [50]. Their primitive apparatus in which they carried out acid-base titration consisted of a common thermometer, a Dewar flask, a stirrer and a hand-operated burette. In the 'twenties, thermometry was tried in all branches of titrimetry, but the breakthrough of the method took place only in the 'fifties, after the invention of low thermal capacity thermistors allowing satisfactorily sensitive temperature recording. In the 'fifties both types of analyses were often published as thermometry [51]. Wasilewski, Pei and Jordan [52] defined in 1964 the principle of direct injection enthalpimetry in "that the change of temperature in an adiabatic system represents a measure of the reactants involved in a stoichiometrically well-defined process".

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Résumé — Examinations thermiques dans l'antiquité et dans le moyen-âge. Méthodes au chalumeau. Mesurage de la température, thermomètres. Chaleur latente. Nature de la chaleur. Analyse thermique différentielle. Analyse calorimétrique différentielle. Traitement thermique des précipités analytiques. Balances thermiques. Volumetrie gazeuse thermique. Thermométrie, enthalpimétrie.

Zusammenfassung — Thermische Untersuchungen im Altertum und im Mittelalter. Die Blasrohrmethoden. Temperaturmessung. Entwicklung der Thermometer. Latente Wärme. Natur der Wärme. Wärmemenge. Differentialthermoanalyse. Differential-Scanning Kalorimetrie. Wärmebehandlung von Niederschlägen. Thermowaagen. Thermogasvolumetrie. Thermometrie, Enthalpimetrie.

Резюме — Термические пробы в античные и средние века. Пробы с паяльной трубкой. Измерение температуры и развитие термометров. Скрытая теплота. Количество теплоты. Дифференциальный термический анализ. Дифференциальная сканирующая калориметрия. Тепловая обработка осадков. Термовесы. Термоаналитические методы, связанные с определением выделенного газа. Термометрия, энтальпометрия.