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SOME INTRIGUING ITEMS IN THE HISTORY OF VOLUMETRIC AND GRAVIMETRIC ADSORPTION MEASUREMENTS

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The short survey concerns the discovery of adsorbents and the measurement of the adsorptivity. In the investigation of adsorption very sensitive instruments are needed, developed only recently. Two methods, however, are very old: the volumetric and the gravimetric measurement of the adsorbed amount. In the Bible we find a thorough description of a volumetric adsorption experiment. The systematic research began in 1773 when Scheele, Fontana and Priestley observed the adsorption of air by charcoal. The volumetric apparatus of Brunauer, Emmett and Teller set the prototype for many instruments devoted to measure adsorption isotherms.

The first gravimetric adsorption measuring instruments were hygrometers, described by Nicholas of Cues in 1450, Alberti and Leonardo da Vinci. In 1833 Talabot installed 39 drying balances in a Lyon laboratory for humidity control of raw silk imported from China. In 1912 Emich described an electronic beam microbalance to investigate adsorption and a coil spring balance. Today isotherms are measured gravimetrically by means of electro-dynamically compensating microbalances. Also oscillating systems are being used which allow weighing down to the zeptogram region.

Keywords: *adsorption, gravimetry, history, humidity, volumetry*

Introduction

Sorption science is new but its roots go back to antiquity when such techniques were already applied without detailed knowledge [1]. Not till the 15th century do we have a more accurate description of water adsorption in the book L'architettura of the Italian architect and painter Leon Battistata Alberti (1404–1472): 'I cannot deny that the humid air of the night is attracted by light earth or penetrates self-acting into the pores in which it may easily condense to wetness'. First, it was all on absorption. Adsorption at the outer and inner surface as opposed to absorption in the bulk was postulated by Kayser on a suggestion of the physiologist Du Bois-Reymond. The use of the term 'sorption' to cover both adsorption and desorption comes from McBain in 1909. The term 'adsorption isotherm' appears to have been introduced by Ostwald in 1885.

The investigation of sorption and the characterisation of adsorbents require sensitive measuring methods and these have been developed only recently. However, two widely used methods to determine the amount adsorbed are already very old: volumetry and gravimetry. Invention and development of quantity measuring tools was stimulated by its need in the early Stone Age when people settled and trade began. Later on also for the preparation of alloys and other chemical compounds proportioning of raw materials becomes necessary.

Adsorbents

Already hominids had fireplaces – the oldest estimated at 1.2 million years old – and produced unintentionally charcoal. We do not know whether they used that first synthesized material as an adsorbent. The first known application of charcoal is as a black colouring material in 30000 years old cave paintings. Recommendations for the use of charcoal as an antidote, and of various adsorbents for drying and disinfecting of wounds are found in Egyptian papyri written before 1500 BC [2] (Fig. 1) as well as in the books of Hippocrates (~400 BC) and Plinius (~50) [3–6]. Adsorbents were used for embalming, washing [7], bleaching, dyeing [8] and as a carrier for paints. Fuller's earth served for decolourisation and clarifying of fat and oil and degreasing of wool [9]. Records concerning desalination of water are found from Thales of Milet (–600), Aristotle (–384—322), Plinius the elder (23–79) as well as in the Bible.

In antiquity two adsorbents were well known: sand and coal. Coal was charcoal, in particular from wood and bones. Sand was, in particular, clay and infusorial earth found in special places. In *Glauberus concentratus* (Fig. 2) [10], a summary of the work of the famous alchemist Glauber, written by a scholar in 1657, we read: 'The best precipitation is performed using a special sand, the origin of which I do not like

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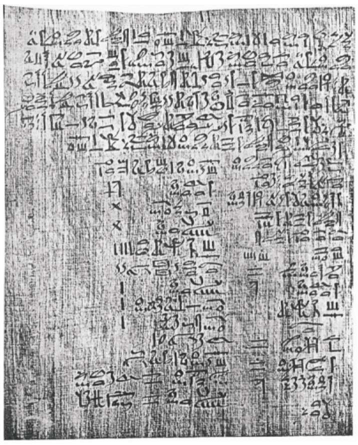
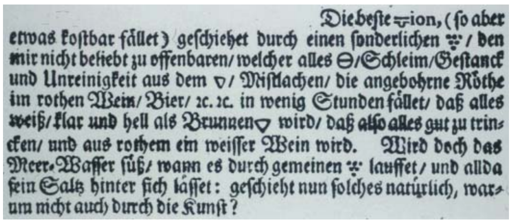


Fig. 1 Papyrus Ebers, page 2, ~1552 BC



Die beste ▽ion, (so aber etwas kostbar fället) geschiehet durch einen sonderlichen ∵/ den mir nicht beliebt zu offenbaren/ welcher alles ⊖/Schleim/Gestanck und Unreinigkeit aus dem ▽/ Mistlachen/ die angebohrne Röthe im rothen Wein/ Bier/ 2c. 2c. in wenig Stunden fället/ daß alles weiß/ klar und hell als Brunnen▽ wird/ daß also alles gut zu trincken/ und aus rothem ein weisser Wein wird. Wird doch das Meer-Wasser süß/ wann es durch gemeinen ∵ lauffet/ und allda sein Saltz hinter sich lässet: geschieht nun solches natürlich, warum nicht auch durch die Kunst?

Fig. 2 Excerpt from Glauberus concentratus oder Kern der Glauberschen Schriften. 1715, Leipzig: Hubert

to reveal. It is able to remove all salt, slime, stench and pollution from water and liquid manor. It removes the innate redness of red wine, beer etc., etc. in few hours so that all becomes clear and bright like spring-water, so that all can be drunk well and that red wine becomes white wine. Sea water becomes sweet if it runs through sand and leaving behind all its salt. When this happens naturally, why not by arts?'

This state of art was expanded not earlier than 1785 when Lowitz discovered the decolorizing effect of charcoal. Subsequently, charcoal was used for the purification first of cane sugar and later on – in the Napoleonic area – of beet sugar. In the 19th century many other applications were invented, but first the patents of Ostrejko in 1900 opened the way for the large-scale production of activated carbon. The first large scale application was in World War I in gas masks and for cleaning air in submarines. Other applications of charcoal became air and gas purification, solvent refining and reclamation, the use as catalyst or catalyst carrier as well as a means to generate a high vacuum. Currently a large variety of new adsorbents are developed and many new applications are found, hopefully for peaceful purposes.

Volumetry

Since more than 10000 years ceramic vessels are produced and most probably used very early also for measuring quantities. A standardisation tablet found in an Egyptian tomb dated about 2620 BC includes drawings of two balance beams and sets of weights and measuring cylinders [11].

The first record of an adsorption experiment we find in the Bible. In the Book of Judges [12] we read: 'And Gideon said to God: If you want me to save Israel by my hand, as you said, behold, I put fresh sheared wool on the floor and if the dew falls only on the wool, and it will be dry at all the earth beside, then shall I know that you want to save Israel by my hand, as you have said. And it was so: When he got there in the early morning and wrung out the wool, he could press out the dew from the wool, a bowl full of water. After that Gideon said to God: Your anger should not flare out against me, if I speak again: Only once more I will try it with the wool: Only the wool shall be kept dry, and dew shall be upon all the ground. And God did so in the following night: The wool remained dry and the dew was on all the ground.' Already Luther remarked that the description of the experiment is unclear. Nevertheless, there are plausible explanations for the inconsistent results [13, 14].

A strange volumetric device should be mentioned which was in use until recently: 'The doctor of Cairo' (Fig. 3). These artistic bowls served for dew sampling during cool nights. The condensed water was used for medical purposes.

For the first time in 1773, Scheele begun to investigate adsorption systematically (Fig. 4) [15]: 'I filled a little retort half with pretty dry ground coal and tied up a bladder. As soon as the retort became hot, the bladder, expanded and when the bottom was glowing, the bladder was not expanding any more. After that, I let the retort cool down, and the air returned from the bladder into the coal. The volume of air was about eight times that of the coal.' Almost simultaneously Priestley in England and Abbé Fontana in Italy measured air by introducing glowing charcoal through mercury into a reversed glass cylinder [16]. On account of the phase transition from the quasi liquid adsorbate into a gas the volume increases nearly by the factor 1000 and thus, the little effects can be measured easily.

Adsorption isotherms were first measured and plotted by Chappuis [17] and Kayser [18, 19] (Fig. 5).

Fig. 3 The doctor of Cairo, a dew sampler

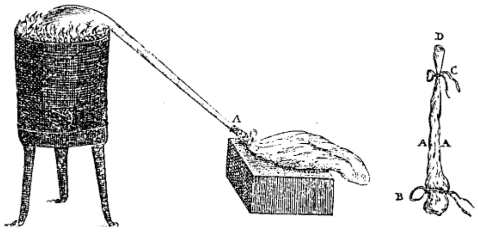


Fig. 4 Scheele's apparatus for the measurement of adsorption. Retort flask in the furnace and a bladder as receiver. At the right hand side an empty bladder

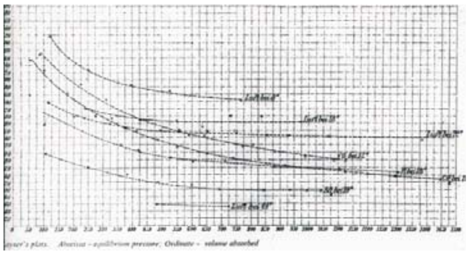


Fig. 5 Adsorption isotherms of H. Kayser

In principle volumetric apparatus is very simple as may be demonstrated by the apparatus of Fischer and Herbst [20] (Fig. 6). The volumetric apparatus of Brunauer, Emmett and Teller set the prototype for many instruments devoted to measure low temperature adsorption isotherms and determining surface area and porosity [21, 22]. The sensitivity of the volumetric method is further improved; modern apparatus are miniaturised and run automatically. Today it is possible to trap individual atoms in a molecular cage.

Gravimetry

The first balance was found in Upper Egypt and is dated pre-dynastic, i.e. it is older than 5000 years. At those times balances were not sensitive enough to measure adsorption effects. The aim of the first gravimetric adsorption measurements was to forecast weather by determination of atmospheric humidity. The very first to describe such an instrument [23] was the German cardinal Nicolaus Cusanus (1401–1463). In his book, published 1450, 'Idiota de Staticis Experimentis' that means 'The layman about experiments with a balance' (Fig. 7) [24] he let this ignorant person, probably his mechanic, suppose: 'If anyone hangs on one side of a big balance with dry wool and loads of stone on the other side until equilibrium is established, at a place and in air of moderate temperature he could observe that with increasing humidity the mass of the wool increases and with increasing dryness of the air it decreases. By these differences it is possible to weigh the air and it is likely that one might perform weather forecasting.'

About 20 years later the Italian architect and painter Leo Battista Alberti (1404–1472) described a similar device: 'We know, that a sponge becomes wet from atmospheric humidity and by this fact we make a balance with which we weigh the weight of the air and the dryness of the winds' [25]. From Leonardo da Vinci (1452–1519) we have three designs of inclination balances loaded with a sponge or with cotton [26–28]. With reflected face he added to the sketches: 'To recognize the quality and density of the air and to forecast rain' and 'Means to detect, when the weather will break-up'.

At the end of the 18th century the metric/decadic system was introduced. In order to realise the kilogram protoype very sensitive balances had been required [29]. In 1861 the first vacuum balance was constructed by Deleuil and used by Regnault to control the mass standards (Fig. 8) [30]. The Deleuil balance in its iron case still exists and is exhibited in the Musée des Techniques du Conservatoire des Arts et des Métiers at Paris. It was the aim of vacuum metrology to avoiding buoyancy. However vacuum desorp-

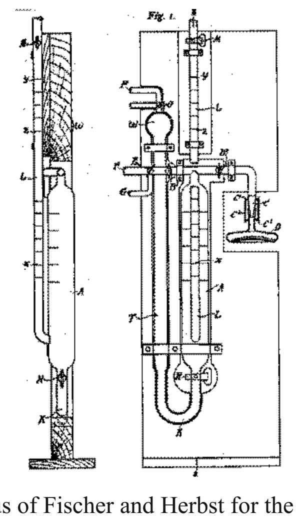


Fig. 6 Apparatus of Fischer and Herbst for the measurement of absorptivity

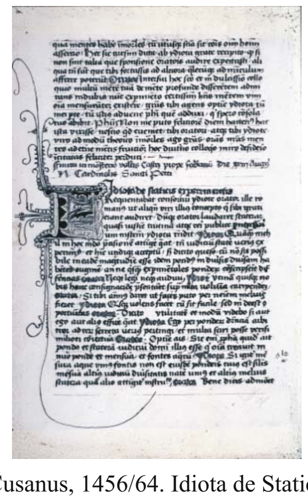


Fig. 7 Codex Cusanus, 1456/64. Idiota de Staticis Experimentis, Folio 132r ff. was completed on September 13, 1450 in Rome

tion of contaminants from the surface of the kilogram prototype caused large uncertainties [31]. In 1984 the Japanese were the first to succeed in comparing standard weights in vacuum with a higher accuracy than in the atmosphere [32, 33].

Thermogravimetry begun with Talabot who in 1833 at Lyon equipped a laboratory with 39 balances for humidity control of silk which was imported from China by ship (Fig. 9) [34, 35]. The whole equipment including the lovely enamel-work shielding the ovens seems to be lost. In 1915 Honda appears to be the very first to use the expression 'thermobalance' for his instrument (Fig. 10) [36, 37]. Soon afterwards such instruments were used to investigate the metabolism of plants (Fig. 11).

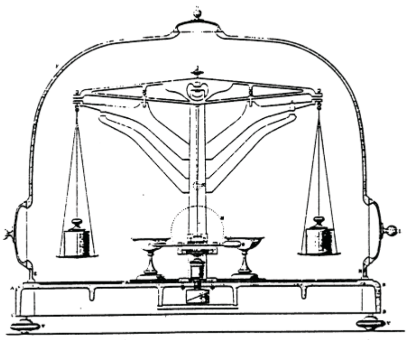


Fig. 8 First vacuum balance: metrological kg-balance of Delieul for Regnault, Paris

Fig. 9 Desiccateur Talabot Rogeat Persoz

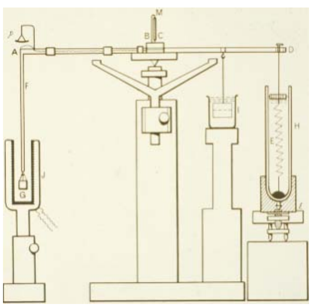


Fig. 10 Honda's thermobalance

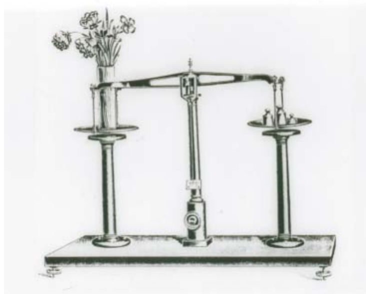


Fig. 11 Measurement of the metabolism of flowers

In 1877 Hannay [38] described a gravimetric method to determine dehydration isotherms of salts. By means of a carrier gas he conveyed water vapour released from a heated sample into a cylinder filled with an ad- or absorbent. That cylinder was weighed periodically. Warming up samples in a heating chamber and sequential measurement of the decreasing sample mass in order to determine the desorption isotherm is still widely used [39, 40]. Today the measurement of humidity is facilitated by so called drying balances: laboratory scales equipped with an infrared or microwave heater [41].

In 1886 Warburg und Ihmori [42] built a beam microbalance for adsorption measurements (Fig. 12). The first vacuum microbalances with electromagnetic compensation were made in 1912 by Emich [43, 44] and Urbain [45]. Today a variety of electrodynamic compensating vacuum microbalances is on the market [46, 47]. Also several apparatus equipped with such

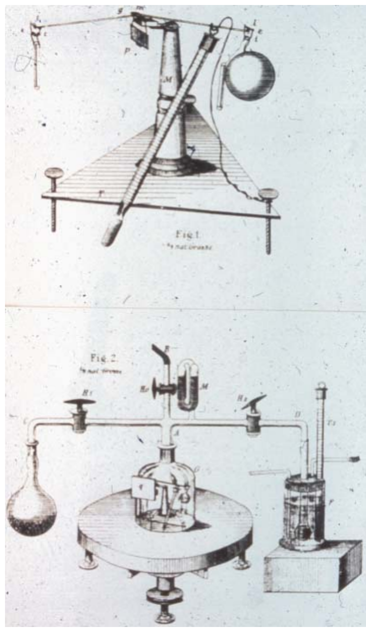


Fig. 12 Vacuum microbalance of Warburg and Ihmori

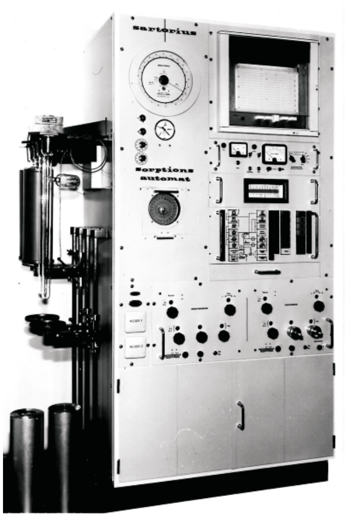


Fig. 13 Sartorius Gravimat of Sandstede and Robens: apparatus for the automatic measurement of sorption isotherms. On the left hand side the electrodynamic vacuum microbalance of Gast

balances for automatic measurement of adsorption isotherms are offered, the first one built in 1962 [48] (Fig. 13).

A quartz fibre spiral spring balance was designed in 1904 by Salvioni (Fig. 14) [49–51]. In 1915 Emich described an apparatus with a helical spring balance for the investigation of microchemical reactions [52]. Such a spring balance arranged in a vacuum tube was applied for sorption measurements by McBain und Bakr [53]. Also an apparatus for surface area and pore determination by means of a spring balance has been described [54]. Though not offered commercially quartz or tungsten spring balances are still used on account of its simple design suitable for work in ultrahigh vacuum and in corrosive atmosphere. It is intended to use a spring body (load cell) with strain gauge as a first balance on Mars. The principal objectives are measurements of the surface structure of Martian soil and its sorption capacity [55, 56].

Favourable for the investigation of adsorption processes are magnetic suspension balances in which the vessel including the sample suspended at a magnet is separated from the balance. In a special case adsorption measurements have been made on particles suspended freely in an electrostatic field [57].

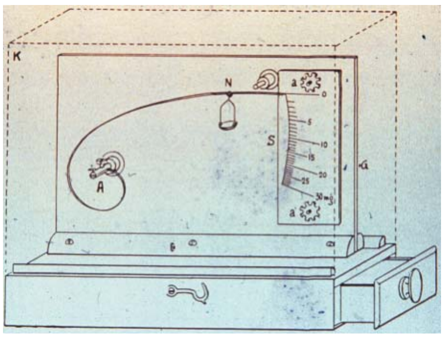


Fig. 14 Salvioni spring balance

An oscillating quartz crystal was used first for adsorption measurements by Wade und Slutsky [58]. Using high frequencies, the method is restricted to measure mass changes of samples which are firmly connected to the sensor. However QCM can be applied to observe adsorption in liquid surrounding. The quartz surface covered with an adsorbing film can be used as a gas sensor. By observing the frequency shift of oscillating carbon nanotubes or of silica nanorods recently, mass variations in the attogram or zeptogram range have been observed. Techniques applied in the atomic force microscope (AFM) can be used to observe the displacement of single atoms.

Conclusions

The volumetric and gravimetric methods of measuring the adsorbed amount and adsorption isotherms have roots going back to antiquity. In the increasing application of processes at the surface of materials such methods become important tools and further development is foreseeable.

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