

CARBON DIOXIDE IN SELF-RISING FLOUR AND BAKING POWDER: A STUDY IN APPARATUS, SCHEIBLER TO CHITTICK

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An important piece of apparatus frequently used by chemists concerned with the composition of baking powder and self-rising flour (hereafter BP and SRF) is one that is able to determine the amount of carbon dioxide (hereafter CO₂) contained in these products. Knowing the amount of CO₂ available to produce properly raised baked goods gives a clear indication of the products' quality and likely performance as a commercially saleable product.

This article traces the evolution of a relatively simple piece of laboratory equipment which to the present time consists mainly of a graduated manometer, or large U-tube, connected to some kind of reaction vessel in which the sample under test can be treated with a suitable acid (or sometimes water) in order to release the CO₂ which is then measured volumetrically.

This apparatus is known as the Chittick and this article traces its development from its earlier relative invented in the 1860s, as a means of determining CO₂ impurity in the sugar refining industry, to its present role in BP and SRF analysis.

“You Can Only Know What Baking Powder Is by Analysing It.”

So claimed the Recorder in a notorious legal case of the Norfolk Baking Powder of 1880 (1). The same dictum could have been applied to self-rising flour since both

products had by this time attained a commercial market place (2). Exactly when analysis began as a service to the manufacture or use of BP and SRF is difficult to ascertain; however, according to Chirnside and Hamence (1974), the appointment of Public Analysts followed from the first Adulteration Act passed in 1860 (3). Also, whenever a commercial product was made, particularly in blended powdered goods, there no doubt came a need to ascertain the accuracy of the manufacturing procedures or processes used. To this end the services of chemists would be drawn into this industry and once established the exchange of chemical knowledge was made available through scientific societies, their publications and related trade journals etc.

Chemists and their apparatus experience mutual development. It seems appropriate therefore to give some account of the entry of chemists into the branch of analysis concerned with food before considering the development of their apparatus for the determination of CO₂.

One important chemist concerned relatively early with the adulteration of food was F. C. Accum (1769-1838) who, in his *A Treatise on Adulterations of Food* (1820), devoted an entire chapter to the adulteration of bread by such chemicals as magnesium carbonate and ammonium carbonate, but mainly alum (4). He cited a *Times* report of October 1819, where mere possession of alum (a favored adulterant) brought legal redress (note on p 131):

... a baker, was convicted ... of having in his possession a quantity of alum for the adulteration of bread, and fined in the penalty of £5. and costs, under 55 Geo. III. c. 99.

The need for analysis of food arose mainly from the medical profession's concern over food adulteration, particularly in commercially processed food where fraud or mere errors of processing might exist. It is no surprise therefore that medical professionals first promoted analytical interests. According to Clare and Clare (2012), it was Thomas Wakley (1795–1862), founder of the *Lancet*, who encouraged A. H. Hassall in 1850 to investigate this subject (5), the results of which initiated legal intervention by means of a Parliamentary Select Committee of 1855 resulting in “An Act for Preventing the Adulteration of Articles of Food and Drink 1860” (6). Meanwhile, Hassall's book *Adulterations Detected* (7) had been published in 1857 and was followed by a further act in 1872 entitled the “Adulteration of Food and Drugs Act.” Local boroughs soon had the right, although not the legal obligation, to appoint Public Analysts as advisers to the regional Medical Officer of Health.

Chemists quickly formed their own society and journal, *The Analyst* (8), from which this article has frequently drawn. The year 1876 thus marked the beginning of food product analysis by professionally qualified chemists who, it should be remembered (9):

... started with almost no knowledge of the composition of food and equally almost no knowledge of reliable methods of analysis.

Prosecutions occurred as the appointment of Public Analysts increased. Liversee (1932), under the heading of adulteration in Effervescent Foods and Drugs, cited only four samples of 76 submitted in the period 1900–1928 were deficient in CO₂ content (10). Adulterants such as alum and calcium sulfate, often in high concentrations, resulted in prosecutions. Those in Britain arising from low CO₂ content included (11):

Lowestoft. Total carbonic acid 4.1%, available carbonic acid 0.85%, instead of 8% of total carbonic acid gas, of which 90% should be available. It was practically devoid of available carbonic acid, the essential ingredient. Fine £2 (*Grocer*, 1907, July 27, Aug. 3; *B.F.J.*, 1907, 138).

Lambeth. Available carbon dioxide 2.4%, instead of at least 6%. ...

Newcastle-on-Tyne. ... The ingredients were only sufficient to yield 2.6% of carbon dioxide, instead of 6% as a minimum.... Case dismissed (*Grocer*, 1916, Oct. 14; *B.F.J.*, 1917, 16).

Mansfield. Carbonic acid gas 4.33% instead of 8% ... Dismissed (*Grocer*, 1917, Dec. 8).

West Ham. Available carbon dioxide 1.1% and of very little value as a baking powder. Fine and costs 61s. (*Grocer*, 1923, June 16).

Wolverhampton. Carbon dioxide 1%, whereas a reasonable percentage was 8% ... Paid costs 53s. 6d. (*Grocer*, 1929, June 8).

Six to eight percent appears to have been an acceptable CO₂ content which is much below present day levels (up to 18%). There was no mention of SRF in this section.

The most important characteristic of BP or SRF is ability to generate CO₂ under conditions of use involving moisture and heat. This property demands accurate measurement—particularly in the case of SRF where the percentage composition of CO₂ is relatively low compared with the bulk of the product. Furthermore, both products can lose CO₂ during storage depending on moisture present within the products at the time of manufacture or taken up afterwards.

Measurement of gas volume has a long history in the annals of science but of course baking powder came into being long after these original researches. Page (2013) identified chemical aspects as part of the early development of BPs and SRFs (12), but it is unlikely that chemists were routinely employed by BP manufacturers in that period.

The eighteenth-century natural scientist Joseph Black (1728–1799) published *Experiments upon Magnesia Alba, Quicklime, and Some Other Alkaline Substances* in 1756 (13) which described decomposition of carbonates to liberate CO₂ using accurate quantitative means (14). Whilst this may appear to have little direct parallel with BP analysis of today, it nevertheless showed that Black faced considerable difficulty in determining CO₂ content by weight. What follows in this article is an attempt to trace the development of the apparatus and methods used to determine the CO₂ content of BPs or SRFs mainly by volume.

One early pioneer, though not at the time concerned with BP or SRF, designed a volumetric means of measuring the volume of gas liberated from the carbonate impurity in bone char, a substance frequently used in sugar refining (16). That invention belongs to Dr. Carl Scheibler (Figure 1, 1827–1899), whose *Calcimeter* is fully described below.



Figure 1. Carl Scheibler (1877). © SDTB: Historisches Archiv. Bestand Zucker-Museum (15).

Analytical Apparatus: A Gasometric Method

The name of Carl Scheibler occurs in chemical literature and the earliest extant copy of his instructions regarding his invention of an apparatus for the sole purpose of measuring released carbon dioxide from carbonate salts when reacted with acid appears in a publication of 1865. This is entitled *Anleitung zur Gebrauche des Apparates zur Bestimmung des kohlensauren Kalkerde in der Knochenkohle, &c.* Dr. C. Scheibler, Berlin, 1865 (17). The title translates as *Instructions for the Use of the Apparatus for Determination of Carbonate of Lime in Bone Char as well as the Volumetric Quantitative Analysis of Carbonate Salts*. No earlier editions of this small book have been found but an 1865 copy is held by the Universitätsbibliothek at the Technische Universität Braunschweig (18). On its title page it is described as a “third edition, enlarged and corrected,” thus indicating two earlier editions, one of which may have been 1862. It is impossible to say whether the other edition came before or after 1862. There is also an 1874 edition held by the German National Library of Science and Technology.

An early textbook citation by Fresenius (1865) described Scheibler’s apparatus fully and its method of use and in a footnote referred to the 1862 booklet by Scheibler (19):

“Anleitung zur Gebrauche des Apparates zur Bestimmung des kohlensauren Kalkerde in der Kno-

chenkohle, &c.,” von Dr. C. Scheibler, Berlin, 1862. (on p. 711)

Scheibler’s reputation as inventor and chemist rested more upon his fame regarding sugars than on the creation of a relatively simple apparatus for measuring gas volume; nevertheless he deserves recognition for what became known as Scheibler’s Apparatus. His life is documented in the *New German Biography* (20), which shows his considerable contribution to sugar chemistry and refining but omits his invention of the gas volume apparatus.

Fresenius’ (1865) comprehensive account described the importance of analysis of bone black (sometimes referred to a bone earth), for this material is used in both the “preparation of beetroot sugar, and in the refining of cane sugar” (p 710). The process of recycling used bone black also made a demand for analytical control. According to Fresenius, Scheibler’s apparatus gained popular use in German sugar manufactories and the account ends, “The process is very expeditious, and in careful hands yields excellent results” (p 714).

Five years later the apparatus was reported in William Crookes’ journal, *The Chemical News*, in an article by William Arnot (21). This writer placed Scheibler’s apparatus firmly in the context of sugar refining as a means of determining the amount of calcium carbonate in bone char (22). Other industries, such as cement manufacture, found use for this apparatus (23) as a means of quantitatively determining calcium carbonate present as an impurity, but its main application lay in assessing the value of the bone-char used in sugar refining and decolorization (24):

The almost daily use, for some years, of Dr. Schiebler’s [*sic*] expeditious instrument for the estimation of carbonic acid in carbonates, and the invariably consistent results obtained, have made it quite a favourite with the author of these notes. Believing the instrument to be far too little known, he would seek to call attention to its value, especially to those who have the charge of sugar refineries, where the frequent estimation of calcic carbonate in animal charcoal is a desideratum.

Arnot also mentioned Fresenius’ description of the instrument adding that “a perusal of the original German instructions will be found profitable” (25).

Crookes gave a full account of Scheibler’s apparatus in his analytical textbook, *Select Methods of Chemical Analysis* (26):

Volumetric Estimation of Carbonic Acid in Solid Carbonates, Animal Charcoal, &c.—Dr. Schiebler [*sic*] has devised a very perfect instrument which is adapted for the estimation of the quantity of carbonic acid contained in native carbonates, as well as in artificial products, and has been specially contrived for the purpose of readily estimating the quantity of carbonic acid contained in animal charcoal. The principle upon which the apparatus is founded is simply this:— That the quantity of carbonic acid contained in carbonate of calcium can, according to well-known stoichiometrical [*sic*] rules, be used as a measure of the quantity of that salt itself; and instead of determining, as has been usually the case, the quantity of carbonic acid by weight, this apparatus admits of its estimation by volume. It is by this means possible to perform, in a few minutes, operations which would otherwise take hours to accomplish, while, moreover, the operator need scarcely possess any knowledge of chemistry. The analytical results obtained by means of this apparatus are very correct, provided care be taken to use the needful precautions (p 390).

From the diagram of Scheibler's apparatus shown in Fresenius' textbook (Figure 2) the actual working of the apparatus becomes obvious.

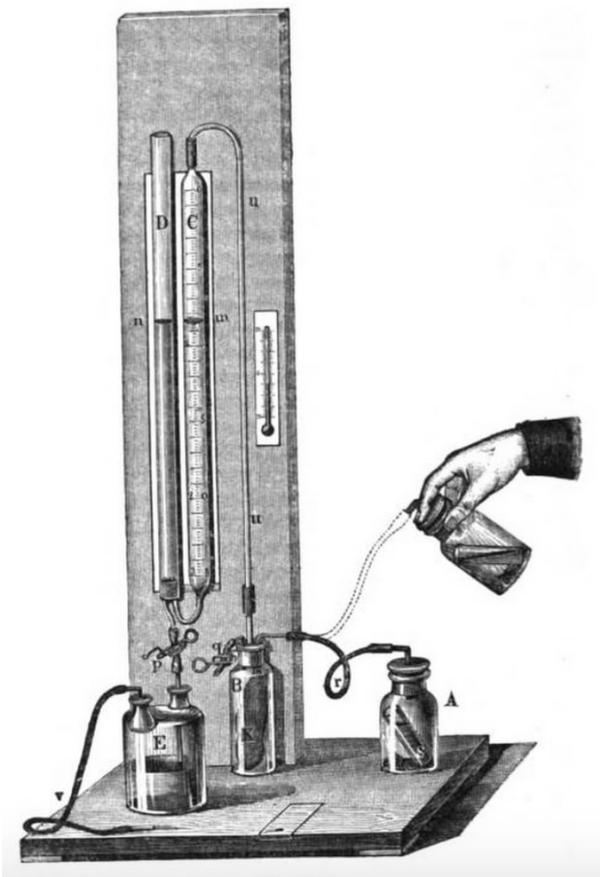


Figure 2. Scheibler's Apparatus from Fresenius (19).

The reaction vessel is on the right and contains the sample plus a loose tube of the acid which when the whole is suitably inclined brings about the reaction. The liberated CO_2 enters a thin india-rubber bladder (27), and the displaced air then depresses the liquid in the right-hand graduated tube (having earlier adjusted both tubes to zero). The levels in both tubes achieve equality by drawing off sufficient liquid into the left-hand vessel in order to attain this state. After the determination the liquid can be returned to the zero marks by blowing through the mouth tube shown. Both tubes are connected to each other acting as a manometer. The graduated tube shows the amount of CO_2 liberated from the weighed sample. Another leading analytical textbook of the period, Sutton's *Volumetric Analysis* (1871), included an account of Scheibler's apparatus (28).

The immediate publicists of Scheibler's apparatus were Fresenius and Crookes and it is surprising that neither paid greater attention to the inflatable bladder within the middle container. Although Scheibler perhaps devised this as a means of avoiding the possible dissolution of CO_2 (or other gas) into the burette liquid—it was clearly a thin-walled bladder (*postpapierdünnem Kautschuk mündet*) as thin as writing paper—neither of these commentators considered the consequences should the balloon happen to fill to more than its “uninflated” or flaccid state. Any additional gas would cause elastic resistance and in so doing the pressure in the bladder would be greater than its surrounds. Such a situation would have inevitably produced an inaccurate burette reading.

The possibility of CO_2 dissolution into the reaction acid had certainly been anticipated by Scheibler who devised a correction factor. Fresenius (1865) also remarked on this point (29):

Schiebler has determined the small amount of carbonic acid which remains dissolved in the 10 c.c. hydrochloric acid at the mean temperature, and he directs to add 0.8 c.c. to the volume of carbonic acid read off. Lastly, the volume being reduced to 0° , 760 mm. and the dry condition, the weight is found.

The point was ignored in Crookes' account of 1871 but in his later editions of *Select Methods* he recommended the adjustment caused by ‘retention’ of CO_2 rather than absorption. He also suggested a means of confirming the correction by carrying out two determinations using pure CaCO_3 ; in the first using 10 cc of acid and in the second only 5 cc and extrapolating accordingly.

Modifications

An important modification was made by Edward Nicholson in 1874 (Figure 3). This removed possible errors arising from the balloon or bladder, such as over-inflation, by completely removing it. Nicholson also ignored the possible absorption of the gas into the burette displacement solution (30). Dissolution into the reacting acid however remained a necessary factor which Scheibler believed he had fully accounted for.

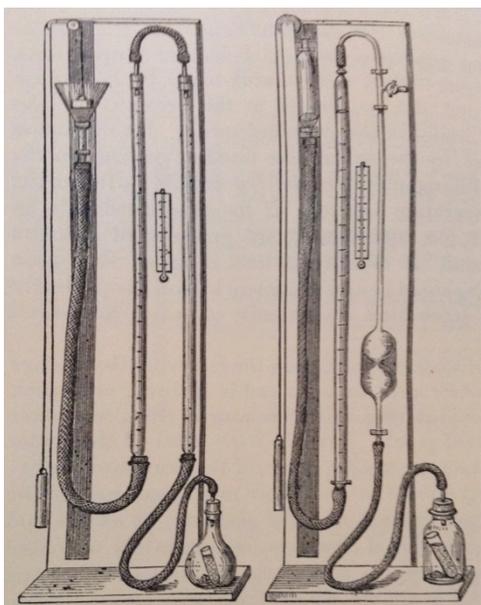


Figure 3. Nicholson's Apparatus of 1874 (31).

Nicholson's new apparatus, which retained the essential features by Scheibler, was reported in *Chemical News* (31). In his short article it appears that he was connected with the Army Medical Department in India and as a consequence had grave doubts as to the efficacy of the india-rubber bladder used by Scheibler. Because of the Indian environment he expressed reluctance to import the apparatus if only because "very thin india-rubber would probably arrive in a glutinous condition." For this reason his modified design removed this possibility and satisfied his need for a quick and accurate method for CO₂ determination.

Nicholson provided a sketch of his apparatus; the left-hand side shows his actual modification for use in India, and the other for construction in "other countries where the manufacture of apparatus is carried on."

Instead of using Scheibler's second graduated measuring tube with reserve bottle and blowing tube he constructed a reservoir capable of moving vertically in

order to maintain equality during liberation of CO₂. The india-rubber diaphragm was thus no longer needed and he assumed there would be no significant "diffusion taking place beyond the double bulb during the short time which the operation requires."

Though much resembling a modern Chittick apparatus, discussed later, Nicholson retained Scheibler's separate reaction vessel with its vial of acid, not realizing that the acid addition could be made easier by merely connecting a separate exterior burette and subtracting the volume used from the actual gas as measured.

A further attempt to improve and make more convenient the use of Scheibler's apparatus appeared in 1877 in *Journal of Chemical Society* (32) in which the authors, Pruen and Jones, mention "Scheibler's well-known calcimeter" but describe their own modified form as a "carbometer" (Figure 4).

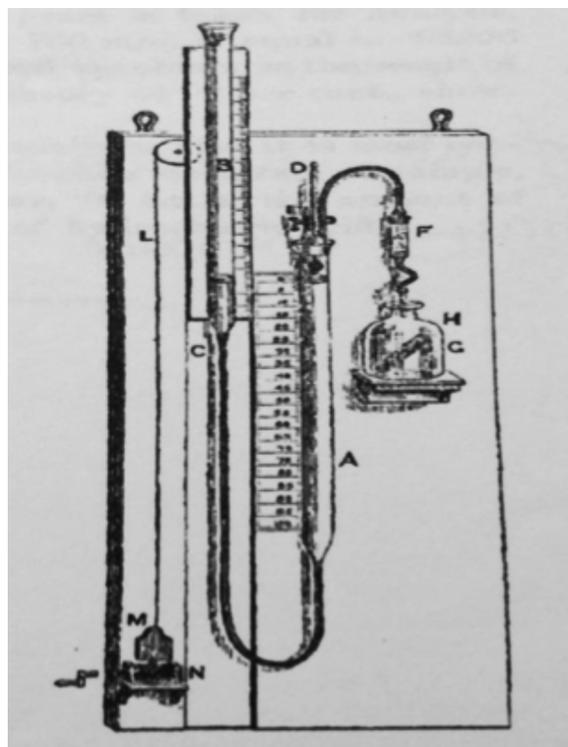


Figure 4. The Carbometer of Pruen and Jones (32).

Using their apparatus they carried out analyses of calcium carbonate in which allowance was made for dissolution of CO₂ into the acid component. This was made on the basis of using "hydrochloric acid, 1 c.c. for each decigram of sample, and to calculate, according to Scheibler, [0].08 c.c. as the amount of carbonic anhydride dissolved in each c.c. of hydrochloric acid" (33).

By this means results were obtained of 43.99% against a theoretical content of 44.00%. CaCO_3 .

In addition to these experimental results the authors describe their major improvement in design of the apparatus by suggesting “two equal and graduated glass tubes, one (A) stationary, the other (B) [the leveling tube] capable of moving in a vertical direction” (similar but offering a slight improvement to the earlier Nicholson apparatus). This advantage becomes obvious and useful inasmuch as there is no necessity to withdraw an amount of liquid equal to the volume of CO_2 generated—as was necessary in Scheibler’s original design. By having the ability to move the leveling tube up or down the levels can easily be brought to equality.

Crookes’ *Select Methods* did not mention Nicholson’s modification of 1874 until 1905 (34), by which time the further changes made by Pruen and Jones in 1877 had been reported resulting in an apparatus much resembling that of the present time. However, all three innovators retained the awkwardness of the separate acid tube within the reaction vessel.

There were several other published articles related to Scheibler’s original apparatus some of which are discussed below. One example, reported by Collins (1906), suggested a means of improving temperature control and disregarded the earlier modifications discussed above (35).

In his article Collins referred to two earlier authors (36) who claimed that with very small amounts of calcium carbonate, 0.5% and below, Scheibler’s apparatus “becomes unworkable, for all the gas produced remains in the reacting acid.” Collins appears to accept these observations but nevertheless regards Scheibler’s apparatus as very vulnerable to temperature variations when compared with other means of gas analysis. To counter this possible source of error he suggested: “... the simplest and most efficient means of obtaining these ends [temperature control] is to bodily sink the apparatus under water, ...” (37). This unwieldy arrangement, surprisingly, appeared in Sutton’s *Volumetric Analysis* even as late as 1935 (38).

In considering the solubility of carbon dioxide in the aqueous acid, Collins provided correction tables and complicated gas equations—much in agreement with Scheibler. Both authors (Scheibler and Collins) also commented on the solubility of CO_2 in the burette water. A further consideration was that of the effect on vapor pressure “of unknown amounts of calcium chloride and other salts” particularly when testing soils, and Col-

lins devised correction tables for when such salts were thought to be present.

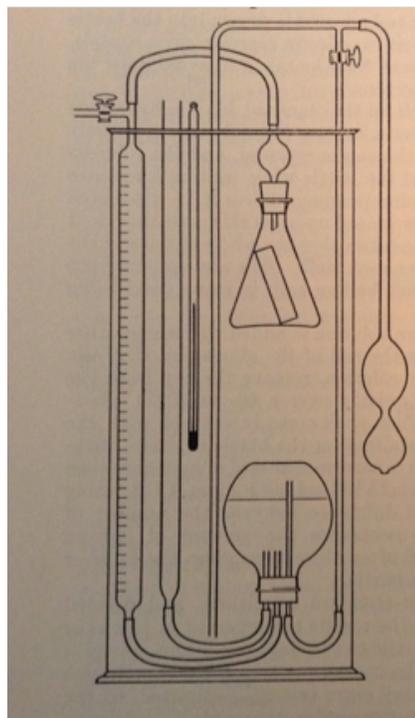


Figure 5. Collins’ Submerged Apparatus (38)

A further criticism of Scheibler’s apparatus appeared in 1898 in the *Journal of the Society of Chemical Industry* (39) in which the author, Arthur Marshall, also points to possible dissolution of carbon dioxide into the acid used in the reaction to liberate the gas (and presumably also the displacement solution in the measuring burette and leveling tube). He points out that because the total volume of gas in the apparatus is substantial, any errors from incorrect barometric and temperature readings could influence accuracy. He claims that a change or error of one degree centigrade could result in an error of 2 cc. of measured gas. Whatever remedies this author had in mind they did not result in any major changes to the existing design but nevertheless reflected contemporary technical concerns.

A publication of 1899 by Catlin (40) promoted the work of Eben Horsford’s 1850s development of phosphates for use in baking powder and also commented on Scheibler’s apparatus. Catlin pointed out that because of its inability to measure large quantities of gas this restricted its use to the determination of CO_2 in bone-char only. To overcome this limitation Catlin proposed the incorporation of a reservoir into the burette or manometer but oddly ignored the easier option by the analyst to

use a smaller sample. Nevertheless, the suggestion had value and implied that Scheibler's apparatus was in use for baking powders at that time.

Absorption Methods

Determination of CO_2 can be achieved by liberating the gas followed by its quantitative absorption. One instance where a method of this kind was first specifically applied to BP is explained in an article by C. A. Crampton (1890) (41). The analytical method he chose was that attributed to A. E. Knorr (Figure 6). This depended upon absorption of the CO_2 into weighed potash bulbs and was a method given in the first edition in 1920 of *Official and Tentative Methods of Analysis* of the Association of Official Agricultural Chemists (A.O.A.C) (42).

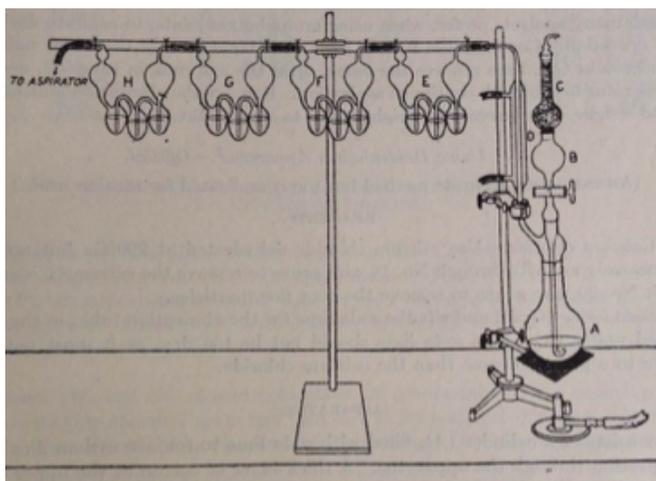


Figure 6. Knorr's Apparatus (42)

Absorption methods remained of importance although cumbersome and time consuming compared with the future gasometric methods employing Scheibler's principle in design. One earlier writer in 1914 (43) gave Knorr's apparatus as the only method at that time for determining both total and available CO_2 in BP. These terms became of importance in Britain when government legislation set controls on CO_2 content in BP and SRF. (See below.)

Crampton's paper above remains of value firstly because it confirms contemporary interest in analysis of baking powder at an early time (1890) and secondly for his use of terms which only somewhat later gained common usage. For example he mentions two distinct measurements, the first, using acid to determine the *total* amount of CO_2 present, and secondly, by the addition of

water only to determine what he called available CO_2 content. In other words (44):

... it is the quantity [of CO_2] which would be actually liberated by the acid ingredient of the powder when it is used in baking, and therefore represents the actual value of the powder for aerating purposes, ...

Two published papers, separated by eleven years (1904 and 1915), are of significance regarding the measurement of liberated CO_2 , for they give some indication of the developing interest in the analysis of SRF and BP. Both articles are by Thomas Macara (45), the second of which, not only from its title but also from the opening sentence, suggest that analysis of these products was already established for "it is customary to estimate the total and available carbonic acid." Both articles describe the same apparatus (Figure 7), which employed a large decomposing flask connected to an absorption flask containing excess baryta as a saturated solution of barium hydroxide. The liberated CO_2 from the reaction vessel passes over into the baryta solution to form an insoluble precipitate of barium carbonate which by using appropriate indicators can be titrated with standard acid.

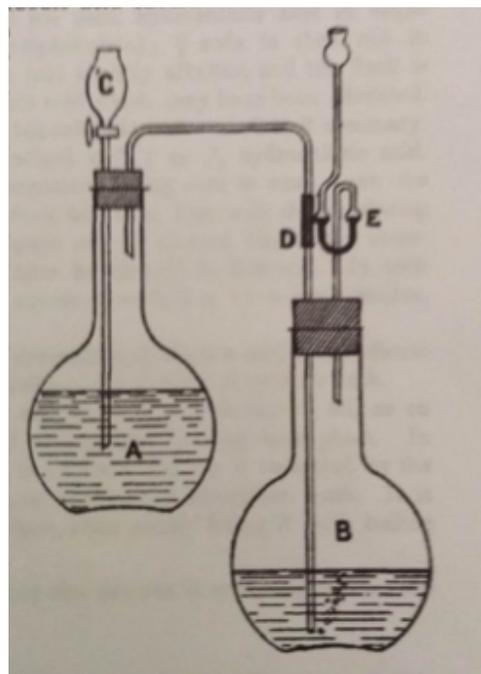


Figure 7. Macara's Apparatus (Ref. 45, 1904).

Macara's description appears somewhat convoluted, however, and his experimental results ambiguous. His method involved firstly precipitating barium carbonate and by several titrations reaching a point of determining the carbonate with acid to methyl orange end point. A simpler method would have been to introduce a known

volume of standard baryta into the absorption flask and to titrate the unused remaining baryta with standard acid to phenolphthalein after the reaction was completed.

Nevertheless, Macara's 1915 paper throws light on a growing interest in analysis of BP and SRF and confirms that analysis of these products was established before the time of his writing. The future legislation concerning this trade will be seen to increase the need for reliable analysis.

Macara's terminology is worthy of examination. For example, his opening sentence 'it is customary to estimate the total and available carbonic acid,' suggests that such analytical differentiations and their procedures were already in being (although no such terminology is evident in his earlier paper of 1904). He attempted to define these terms more accurately by stating that total CO_2 results from reaction of the BP or SRF with acid, and that available carbonic acid is generally assumed to be that liberated on adding water only to the mixture. However, for some unstated reason he assumes an excess of bicarbonate is usual in baking powders—but there is no reason to believe that makers of BP or SRF were not aware of the desirability of a chemical reaction leading to neutrality. Remember that Crookes spoke of "well-known stoichiometrical [*sic*] rules" in 1871 (46) leading to a neutral and complete reaction. Any possible excess of NaHCO_3 was perhaps due to faulty weighing or an erroneous recipe by the manufacturer or blender, resulting in an unexpected measure of available CO_2 . Thus, Macara believed that available CO_2 ought to be that amount liberated during the entire course of baking. This takes into account the effect of any acid present in the flour, milk or other components in the recipe. From this perspective Macara suggested a modified definition of available CO_2 , namely on the basis of total amount of gas liberated from the normal acid-alkali reaction, (47):

... *plus* that liberated by any acid present in the flour, milk, or other ingredients used, together with that liberated by the action of heat on the excess [if present] of bicarbonate.

He thus proposed a new term, "apparent" available CO_2 (by boiling with water only) and for its determination by his method described earlier in 1904 (48). He further suggested a method "for the estimation of the non-available carbonic acid [residual CO_2], by adding acid to the residue [in the reaction vessel] and boiling into another absorption flask" (49).

It will be seen later that legislation regarding BP and SRF adopted these definitions and because of the framing

of new legal requirements changes occurred in definition. Whilst total CO_2 remained as that volume liberated by adding an excess of acid, a new determination came into being entitled residual CO_2 . This was the amount of CO_2 generated from an aqueous dispersion of the SRF or BP held at boiling point for a fixed time period and then treated with acid. The true available CO_2 was then judged by subtraction of one from the other.

Before considering the currently used gasometric method embodied in the apparatus known as the Chittick, one novel method devised in 1914 is worthy of comment—if only because its title confirms practical interest in the analysis of BP. The principle of the apparatus depended upon generation of CO_2 in a reaction flask and then leading the gas to a saline-filled glass cylinder where the displaced solution was collected in a conventional measuring cylinder. One could reasonably assume too many variables in this apparatus, but nevertheless the author wrote (50):

simple in principle, requires an apparatus simple to construct, and manipulate, consumes little time and gives reasonably accurate results.

In the early 1920s there was a growing interest in more convenient methods of CO_2 determination in BPs caused perhaps from the awkwardness of the two existing official absorption methods (Knorr and Heidenhain) adopted by the American Association of Official Agricultural Chemists (51). This was reflected in a 1920 meeting of this association reported by Robinson and Bandermer (1922) in which an obscure gasometric method, based on a modification of an existing method of CO_2 determination in blood plasma, was suggested for use in BP analysis (52). The complexity must have completely ruled out this method but nevertheless the article showed active interest to find a convenient gasometric or volumetric method applicable to BPs.

The Chittick Apparatus

This apparatus now known as the Chittick was reported in the *Journal of the Association of Official Agricultural Chemists* in 1923 (53) but received its formal approval as a "Gasometric Method.—Tentative" in the 1925 edition of the AOAC's book of methods (54) and is shown in Figure 8. The journal entry shows Chittick's submission:

A volumetric method and apparatus for determining the carbon dioxide content of baking powder. (Submitted by J. Raymond Chittick). (p 453)

Chittick provided instructions on the determination of residual CO_2 by reacting the sample fully with water followed by reaction with acid in his apparatus, thus obtaining an available CO_2 content by subtraction from the total content. The report ends in the recommendation that the accuracy of the method “be compared with the official absorption methods before they [volumetric methods] are recommended as tentative methods.”

In 1930 three authors, Chittick, Dunlap and Richards (55), published a paper in answer to criticism of the apparatus made by Hertwig and Hicks two years earlier (56). They claimed inaccuracies of the Chittick method related to vapor pressure of the acid solution. The two groups based their arguments on different publications of the Chittick method (57), but there appears to be no significant difference of method between them.

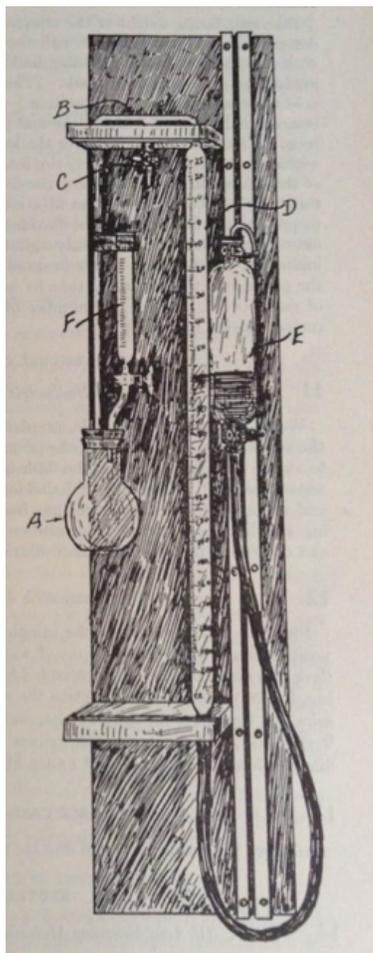


Figure 8. Chittick Apparatus (AOAC 1925, Ref. 54)

Chittick *et al.* began their reply by describing the essentials of the method (58):

... the method depends on the liberation of the carbon dioxide from a baking powder by the addition of an excess of sulphuric acid and collecting the gas liberated (or its equivalent volume of air). This gas volume is then reduced by calculation to the standard temperature of 0°C . and 760 mm. pressure. Knowing the weight of one cubic centimetre of carbon dioxide under these conditions as well as the weight of the sample taken, the percentage of carbon dioxide in the sample can be calculated.

However, Hertwig's and Hicks' criticism claimed inaccuracies in the Chittick method, not addressed by the AOAC, insofar as the vapor pressure of the added acid must cause an increase in measured volume of gas.

This appears to have been the only major criticism of Chittick's design although the solubility of CO_2 into the reacting and displacement solutions had often received attention even from the time of Scheibler's earlier first account in 1862. Their criticism demanded attention and it was incumbent upon Chittick and his colleagues, as instigators of the method's adoption by the AOAC to respond in the way now described. It was probably the first occasion in which vapor pressure had been publicly discussed in connection with the apparatus. Chittick's response concurred with the criticism insofar as (59):

... when a given volume of dilute sulphuric acid is added to the dry reaction flask, the gas-measuring tube volume will read greater than volume of acid added to the flask, and that this increased volume is due to the vapor tension of the acid.

However, he tempered this fact by pointing out that:

The strength of the sulphuric acid does not remain the same, ... and we have the complex result of the vapour tension of the dilute acid plus the various salts that may be present. This condition undoubtedly does produce a vapour tension but certainly we cannot assume it as being equal to that produced by the acid per se.

Hertwig and Hicks had claimed an increase in the gas volume of “about 3 to more than 5 cc.” (56).

Chittick *et al.* had carried out an extensive program of analyses based on BP samples of accurately known composition and CO_2 content. Indeed this was at the heart of their rebuff to Hertwig and Hicks (who lacked such supporting evidence for the method). All parties acknowledged the presence of a vapor tension, but Chittick claimed the added existence of a compensating factor which must have accounted for the accurate results they consistently obtained in their program of analysis.

Chittick's reply therefore rested upon this compensating factor, and claimed (59):

This is actually the case and the compensating factor appears to be the amount of CO_2 that remains dissolved in the liquid in the reaction flask.

To illustrate this factor Chittick determined the amount of residual CO_2 remaining in the reaction flask by first aspirating away any gas above the liquid and then by connecting the flask to a Knorr's apparatus. On the results so obtained Chittick claimed (60):

... it bears out the point that there is a factor in the CO_2 dissolved in the liquid in the flask which compensates for the vapour tension of the liquid itself ...

Working with highly purified NaHCO_3 these three authors each conducted determinations of CO_2 in BPs of known composition under varied controlled conditions. Having in mind that vapor pressure is reduced with lowering of temperature and that solubility of CO_2 in the flask increases, their results showed these factors working together, and so reducing the gas volume. They claimed therefore the Chittick method's accuracy, even in different hands, and that Hertwig's and Hicks' assertion that a correction factor was necessary was without foundation. Hence (61):

Whatever vapour tension effect is produced by the liquid in the reaction flask is closely compensated for (in the working temperatures generally experienced in the laboratory) by the CO_2 dissolved in the liquid.

Chittick's arguments in response to Hertwig and Hicks' criticism therefore rests mainly upon the fact that the apparatus recorded a quantity of liberated CO_2 exactly equal to that theoretically expected from the prepared sample(s) of BP.

It may appear surprising that Chittick had not earlier considered the effect of vapor pressure and was content to accept the accuracy of the apparatus merely only on the basis of results obtained from accurately prepared BP samples. The apparatus was adopted by the American AOAC though only as a tentative method sometime before 1925 (62) and yet the matter of vapor pressure had not been addressed until raised by Hertwig and Hicks two years later. Of course Chittick's use of an external acid burette, although proving more convenient than by introducing the acid in a separate phial or test tube, made no difference to the effect of vapor pressure.

Little is known about Chittick (63) or the development of his apparatus prior to its adoption by the AOAC, whose early editions of method books do not refer to the apparatus by his name. Nevertheless, the apparatus

bears his name to the present time and remains a standard piece of analytical equipment in many laboratories and is available commercially. Of course the role of the AOAC was to offer reliable and accurate methods of analysis without theoretical discussion and it was in order to maintain the "tentative" position and perhaps his own reputation that Chittick *et al.* were drawn into the aforementioned dispute which he so fully answered. It is known that Chittick was in the employ of the Jacques Manufacturing Co. of Canal Street in Chicago—one of very many baking powder companies in America at that time (64), and presumably it was during his employment here that the apparatus was devised.

The Acidic Ingredient

The rate at which a BP or a SRF releases its CO_2 became of interest particularly when the range of available acidic ingredients included acid phosphates. Although sodium bicarbonate (NaHCO_3) has always retained its position as the source of CO_2 the acidic counterpart received considerable attention if only because the rate of reaction was found to vary from one acid to another, thereby offering the user, the baker, more operational scope in the baking procedure. This subject was highlighted in a 1939 journal notice of a presentation by R. S. Potter and H. H. Bagnall (65), who erroneously dated the use of cream of tartar and monocalcium phosphate as patented by Horsford in America (66).

Acid sodium pyrophosphate was also discussed by these authors, who confirmed its availability commercially as a slow-acting acid but caused "certain difficulties in determining 'available carbon dioxide'" in BPs (67). Potter's and Bagnall's experiments showed that the standard method set by the AOAC (meaning the gasometric using the Chittick apparatus) failed to give sufficient accuracy. These authors also expressed criticism of methods involving absorption into baryta solution followed by titration. They therefore suggested that the means to determine available CO_2 should be more directly related to the complete baking cycle. Though sound in principle it should be remembered that much earlier the AOAC had clearly defined available CO_2 (68):

Available Carbon Dioxide.—Official.

Subtract the residual carbon dioxide from the total carbon dioxide.

Potter and Bagnall tested four different BPs using different acid ingredients to give a theoretical CO_2 content of 14%. The Chittick method registered 11.6%-

13.3%, while a baryta absorption method gave near theoretical results only when testing samples containing quick-acting ingredients. BPs containing slow-acting acidic ingredients registered about half of theoretical. Because of these poor results the authors recommended a method that involved heating the sample in water to 100°C, drawing the liberated gas through 0.3-N baryta, and determining the amount by titration with HCl. The results were consistent within 0.1 ml. of 0.5-N HCl “irrespective of the nature of the acid ingredient” and “it was concluded that the incomplete evolution of gas was due to the weak acidic properties of cream of tartar and sodium pyrophosphate in dilute solutions” (69).

It should be noted however that these authors, finding an uncertain result from the Chittick apparatus, were in fact only initiating the reaction with water (as in the actual baking process). Potter’s and Bagnall’s results, based on known theoretical CO₂ contents involving BPs employing different acidic ingredients, clearly showed the Chittick apparatus was not suitable for tests merely employing water to bring about the reaction. It must be noted however, that these authors were somewhat behind the times inasmuch as the 1925 AOAC *Official and Tentative Methods of Analysis* had (p 306) described reliable means of determining residual CO₂ content—even by using the Chittick apparatus! Nevertheless, they illustrated the relationship between solubility or “strength” of the acidic ingredient and rate of reaction.

Potter and Bagnall made their presentation in 1939 just before World War Two influenced the analytical procedures for BP and SRF. It should be noted that the Chittick apparatus, with only minor adjustments, can be used to give an indication of rate of reaction in BPs and SRFs. By standardizing the agitation of the reaction vessel and controlled addition of water the timed evolution of CO₂ can easily be recorded graphically.

Some Legal Aspects

Analysis is a quantitative pursuit and as such seeks to relate its findings to the compositional requirements set by the manufacturer of commercial products such as BP and SRF, or those standards as decided by governmental legislation. The analytical figures sought by industry may not always be entirely compatible with the aims decided by government regulations. It therefore seems worthwhile to examine how legislation, its context and mode of enforcement, influenced analytical techniques in the BP and SRF industry.

In 1944 two statutory orders regarding the amount of CO₂ evolved from these products came into being (70). Both dictated that available carbon dioxide in BP should be not less than 8% and residual carbon dioxide not more than 1.5% (Golden Raising Powder to yield not less than 6% available carbon dioxide and not more than 1.5% residual carbon dioxide). For SRF the available CO₂ should not be less than 0.45% and total CO₂ not more than 0.65%.

These regulations arose from wartime shortages and were used as a means of limiting the consumption of food phosphates. However, both regulations were ultimately revoked (71), although a 1970 Food Standards Committee report suggested that the trade favored the continuation so far as baking powder was concerned.

The analytical methods given in these orders were somewhat inadequate and contained no reference to the Chittick apparatus. Available CO₂ content was calculated as the difference between total and residual without any specific complete analytical methods quoted. Any consequent trade dissatisfaction following these regulations was considered later by a government subcommittee which included public analysts and industrial chemists.

According to an editorial article in the *British Food Journal* (1946) greater standardization of method was a major requirement by trade chemists, Public Analysts and consultants in view of “meagre instructions for the determination of available carbon dioxide” and consequent poor standardisation from one laboratory to another (72). In fact the new order that followed in 1946 contained little improvement and still made no mention of the Chittick apparatus. Indeed, the new order concerned itself mainly with CO₂ content although the committee’s demand to abandon the upper limit of 0.65% total CO₂ in SRF was accepted. It was of course because of the possible need to control phosphate usage that the 1944 order came into being although it also safeguarded the customers’ interests. Nevertheless, the new order of 1946 for SRF specified no limit on total CO₂ but stated “... flour shall yield not less than 0.40 per cent. of available carbon dioxide” followed by the most basic instructions of analytical method. This gave wider scope to manufacturers in that, without an upper limit, they could, where necessary, formulate to take into account loss of CO₂ in storage. The change also removed any problems arising from the addition of chalk (*Creta Praeparata*) to milled flour following the legal requirements of 1943 in order to increase calcium levels in the diet (73). This of course increased the amount of CO₂ measured by the Chittick apparatus (as total CO₂). The value of the residual content determination in SRF

therefore became of greater significance in order to arrive at a true available CO_2 content and thus avoid possible prosecution. Fortification of flour with vitamins and calcium remains a requirement to the present time.

Argument over available CO_2 content persisted, however, and the 1944 earlier order specified a minimum of 0.45% whereas the manufacturers wanted 0.35% CO_2 in the belief that this was generally sufficient for most baked goods. Arguments flowed to and fro with the submission of cakes and other baked items as support from both sides. The committee finally agreed with the Ministry on a figure of 0.4% available CO_2 cited in the new order of 1946 (74).

Both 1944 and 1946 orders made analytical demands. One single total CO_2 figure was insufficient for a manufacturer to avoid prosecution, thereby giving importance to the determination of residual CO_2 .

The 1946 order still did not specify the full analytical method. The preparation of the sample prior to analysis and the choice of method remained with the analyst. Of course it is not the responsibility of legislative bodies to devise and instruct on analytical procedures. One method, not mentioned earlier in this article appears in the official orders (1944 for both BP and SRF) is merely referred to as “by means of reduced pressure.”

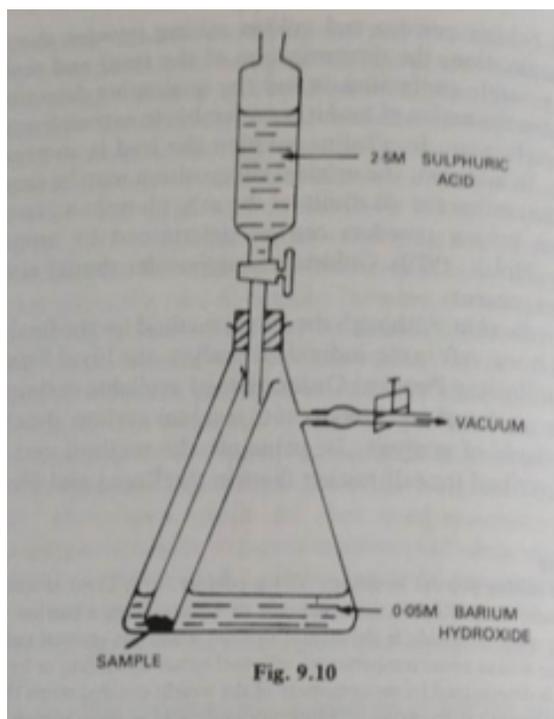


Figure 9. Determination of CO_2 under reduced pressure (75).

Pearson's (1991) (75) illustrates this method (Figure 9). It is self-explanatory inasmuch as the reaction flask is first evacuated, allowing evolved CO_2 to react with the standard baryta solution which after a lengthy standing time is back titrated.

In summary the three general methods consisted of

1. gasometric (Chittick)
2. gravimetric (absorption into soda-lime tubes, though considered insufficiently accurate).
3. volumetric (absorption into baryta solution and titration).

For most modern laboratories dealing with BP and SRF analysis, the Chittick is the choice of apparatus



Figure 10. An everyday working Chittick. (Courtesy of Kudos Blends Ltd.)

(Figure 10) mainly for total CO_2 determination, and it is regarded as the standard method. Relatively easy to operate and giving reproducible results, the aspect of solubility of the CO_2 in the reaction liquid and any vapor pressure present is usually ignored in line with Chittick's argument discussed above.

Because of the legislative changes discussed above the so-called residual CO_2 remained a requirement during the period of regulation and hence the volumetric method, involving absorption of CO_2 into baryta solution followed by titration, was of importance as a means of obtaining the available CO_2 content (by difference) and so avoiding prosecution. The diagrammatic presentation of this apparatus for residual CO_2 determination was given by Kent-Jones and Amos (76) over many editions of their text book is shown in the Figure 11. Industrial laboratories tended to make their own modifications of this apparatus, for example Kent-Jones and Amos (1967) appear rather over-cautious regarding the inflow of CO_2 -free air. The absorption vessels can be easily simplified in order to achieve equally reliable but easier titration.

A current of air is drawn through the residual CO_2 apparatus as shown in the diagram by connecting an aspirator to the second absorption bottle and titration of the baryta standard solution contained therein after evolution of CO_2 from the main reaction flask. This apparatus and the Chittick remained the mainstay of many industrial bakery-related laboratories during the period of legislative regulation; the Chittick however still holds a position of high importance in this area of analysis.

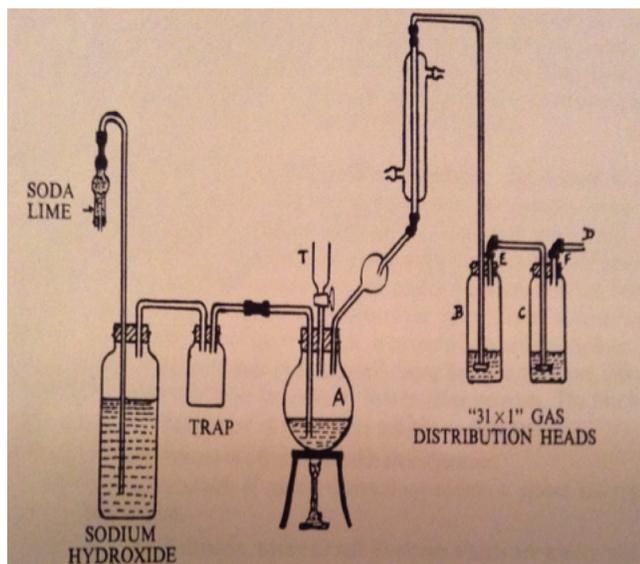


Figure 11. Residual CO_2 Apparatus (76).

Conclusion

Journal articles, in particular by Crampton (41), suggest that analysis of BP was practiced as early as 1890 and possibly before. That such early interest existed is further shown by the 1914 paper of H. W. Brubaker whose apparatus, though designed for the determination of CO_2 in BPs was also, rather unexpectedly, used for the enlightenment of girls in household chemistry (50)!

The exact dating of Chittick's design has proved difficult and requires further research but its entry into the published AOAC methods of 1925 and its earlier journal reporting of 1923 clearly show that it was well established in that period. No records have been found which describe the circumstances under which J. R. Chittick developed the apparatus as we know it today. His employment by a notable BP manufacturer no doubt influenced his achievements. The development of Chittick's apparatus followed from the earlier designs of others influenced by Scheibler's original model. Of course Scheibler was only concerned with its use in his own specialized field of sugar manufacture as a means to determine carbonate impurities in bone char.

It is not obvious why Scheibler used a "thin balloon" in his apparatus but his reason may have been to avoid possible dissolution of the liberated gas into the burette or manometer liquid. It could be asked however why he did not realize that once saturated with CO_2 no further dissolution would occur. Perhaps his cautious approach arose from the belief that this CO_2 -saturated liquid might alter during periods of disuse or because of changes in ambient laboratory conditions. Of course early collection of gases often employed animal bladders and perhaps Scheibler was merely acting within tradition.

This article has illustrated several important modifications to the early apparatus of Scheibler, often not adopted, but usually following his principles of design. Absorption methods have been discussed in this article but these never reached the ease of performance given by the gasometric apparatus from the time of Scheibler to Chittick. Arguments regarding the accuracy of the Chittick apparatus have sometimes influenced its early development, but, as is often the case in industrial analysis, if the measured quantity (of CO_2) matches that of a known prepared sample then further enquiry takes second place.

The modern apparatus in any bakery analytical laboratory would be immediately recognized by Scheibler, though no longer bearing his name. One element of surprise would no doubt have arisen from today's manu-

factured price of around £2,500 compared with £3 for Scheibler's original model. The piece has not changed dramatically although its ease of use is greatly improved since its first invention. The apparatus has retained its main principles through a period of unprecedented instrumentation in industrial analysis as a consequence of the present electronic age (77) and still consists of a reaction vessel connected to a manometer.

Like few other specialized pieces of laboratory equipment the Chittick apparatus has not been replaced by a modern electronic alternative and remains an essential laboratory piece.

Acknowledgments

I am grateful to Frank Moll-Seiler, Librarian, Universitätsbibliothek, TU Braunschweig for information regarding Scheibler and the portrait of Scheibler, courtesy of © SDTB: Historisches Archiv, Bestand Zucker-Museum (15).

I express thanks to the Royal Society of Chemistry for permission to reproduce illustrations from *J. Chem. Soc.*, 1877, (Pruen and Jones' apparatus), and from *Analyst*, 1904 and 1915, (Macaro's apparatus). Permission to reproduce AOAC illustrations has been given by AOAC INTERNATIONAL.

I am grateful to the staff and chemists of Kudos Blends Ltd. Cleobury Mortimer, DY14 8SY. UK, and the Bodleian Law Library, Oxford, Official Papers Librarian, Hannah Chandler, and staff of the Radcliffe Science Library.

Professor W H Brock is thanked for his reading of this manuscript.

References and Notes

1. A report of this legal, if humorous, case was reprinted as, "The Norfolk Baking Powder Case," *Analyst*, **1880**, 5, 21-33. See also, "Alum in Bread," *Br. Med. J.*, **1880**, 1(995), 138.
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9. Ref. 5, p 49.
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12. Ref. 2 (Page).
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16. Bone char is produced by charring animal bones in limited air supply. The product may contain up to 10% carbon.

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18. The book resembles an instruction manual of 27 pages with 7 additional tables and measures 13.5 cm by 20.8 cm, and it is from this source that this article draws. Digitised copy at <http://www.digibib.tu-bs.de/?docid=00059656> (accessed Mar. 26, 2017).
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28. F. Sutton, *Volumetric Analysis: A Systematic Handbook of Volumetric Analysis*, Churchill, London, 1871, 2nd ed., p 364. Not unexpectedly, Scheibler is not reported in the first edition of 1863. In later editions the author reported the modifications recommended by Collins (Ref. 35).
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58. Ref. 55. This description agrees with that given in *J. of A. O. A. C.*, *10*, (1927), 36, to which the authors refer.
59. Ref. 55, p 475.
60. Ref. 55, p 478.
61. Ref. 55, p 480.
62. The first edition of *Methods of Analysis* was published in 1920. The preface described the vigorous process by which a method or apparatus was “tentatively” adopted by a referee whose report appeared in the *Journal* of the AOAC, and that “... a method can be made official only after the most thorough series of tests, not alone for accuracy, but for ease of operation as well.”
63. J. Raymond Chittick was born in the early 1880s in the state of Iowa (US Census data). The Iowa Official Register for 1906 lists him as a member of the chemistry faculty at Highland Park College in Des Moines. He joined the American Chemical Society in 1908, according to a 1935 ACS directory. The Iowa Official Register for 1913-1914 lists Chittick as Chief Chemist under the Dairy and Food Commissioner. He moved to the Chicago area, where he worked for Jaques Manufacturing Company, makers of KC Baking Powder. Jaques was given as Chittick’s affiliation in AOAC reports in the early 1920s, and according to *The Cook’s Book* (a 1933 recipe book published by Jaques, available online at http://archive.lib.msu.edu/DMC/sliker/msuspccsbs_kcba_jaquesmanu8/msuspccsbs_kcba_jaquesmanu8.pdf (accessed Apr. 30, 2017)) he was Chief Chemist. After retirement, he moved to La Jolla, California, where he died in 1950 (“Necrology,” *Chem. Eng. News*, **1950**, *28*(45), 3911).
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65. *J. Soc. Chem. Ind.*, **1939**, 58, 76-77.
66. There are eighteen patents in Horsford's name (some jointly with G. Wilson) but the one of significance here is probably no. 75,336, dated March 10, 1868, regarding the manufacture of phosphates and extracting phosphoric acid from bones.
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69. Ref. 65, p 77.
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71. Revoked in 1984 by The Bread and Flour Regulations 1984 (SI 1984/1304), Schedule 7, Regulation 16, (revocations) in Statutory Instruments, 1984, no. 1304, on p. 4071, following the recommendation of the Food Standards Committee Report on the Pre-1955 Compositional Orders Concerning Baking Powder and Golden Raising Powder etc. p 8, HMSO London, 1970. There were additional revocations in 1995 (SI 1995/1302) and again in 1998 (SI 1998/141).
72. *Br. Food J.*, **1946**, 48(4), 149-158.
73. The Calcium Flour Order became mandatory for the addition of chalk to flour. According to E. N. Greer, J. D. Mounfield and W. J. S. Pringle, "The Estimation of Added Calcium Carbonate (Creta Praeparata) in National Flour," *Analyst*, **1942**, 67, 352-355, the amount added was 7 oz. of chalk to a 280 lb sack of flour. This would add only 0.07% CO₂ (approx.) to the total amount. Small though this was it could have been of significance to a SRF manufacturer.
74. Statutory Rules and Orders, 1946, no. 157, vol. II, pp. 26-27, HMSO, London.
75. R. S. Kirk and R. Sawyer, *Pearson's Composition and Analysis of Foods*, 9th ed., Longman, Harlow, Essex, 1991, p 339.
76. D. W. Kent-Jones and A. J. Amos, *Modern Cereal Chemistry*, 6th ed., Food Trade Press, London, 1967, p 640, and other editions.
77. See Ref. 14, p 291.

About the Author

After retiring from the chemical industry in 1989, the author gained a M.Sc. degree at the Oliver Lodge Laboratory of the University of Liverpool. His studies of early analytical chemistry under the supervision of Professor W. H. Brock resulted in his earning a doctorate from the University of Leicester in 1999. This present article and a previous one in this journal regarding self-rising flour and baking powder, originated from his early employment with Albright and Wilson Co. and involvement with the development of food phosphates.

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