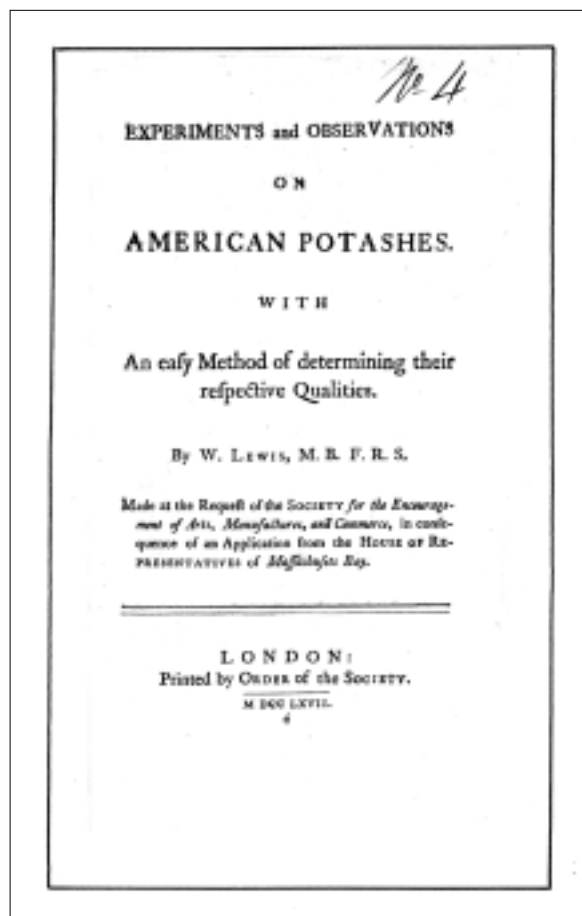


## THE BIRTH OF TITRIMETRY: WILLIAM LEWIS AND THE ANALYSIS OF AMERICAN POTASHES

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William Lewis (1708-1781), was a physician, author, and an experimental chemist. Sometime after 1730 he gave public lectures in London on chemistry and the improvement of pharmacy and manufacturing arts (1). With a growing reputation as a chemical experimentalist he was elected F.R.S., on October 31, 1745, and was then living in Dover Street, London. In 1747 he moved to Kingston-upon-Thames, where he set up a well-equipped laboratory and presumably continued in medical practice. From about 1750 until his death in 1781 Lewis employed Alexander Chisholm as his assistant in chemical and literary works (2). These improved the knowledge and practice of pharmacy, but as a practical consulting chemist Lewis has received little biographical recognition. He was awarded the Copley Medal by the Royal Society in 1754 for researches on platina (platinum), which he claimed was a distinct metal, and for devising methods of chemical identification. These results were published in *Philosophical Transactions*, 1754 and 1757 (3).



In order to place Lewis's work in the context of the early beginnings of the industrial revolution in Britain, Sivin (4) has used a chronological argument; he cites Ashton's suggestion (5) that 1782 was the beginning of the industrial revolution because in that year most statistics indicated a sharp increase in industrial production. But, as Sivin argues, it seems reasonable to assume that by the time such early statistics became available, those industries that had created salable products had already become established and were no longer in their early years of founding. On this basis the industrial revolution must have begun earlier. By the middle of the eighteenth century the social and economic demands of a greatly increased population more probably heralded this dramatic change, visible in the growing demands on the textile, metallurgical, and ceramic industries, all of which required chemicals. Clow relates this birthdate, 1760 to 1780, with the increased number of

registered patents as a barometer of the new industrial activity (6). This places Lewis's analytical developments in a key position relative to the early industrial revolution.

His considerable and yet little recognized contribution to quantitative chemical analysis is best seen in his work on American potashes in consultation with the Society for the Encouragement of Arts, Manufactures, and Commerce. The analytical methods he devised foreshadowed what later developed into titrimetric analysis, and for this work Lewis was awarded the Gold Medal of the Society in 1767.

The Society's archives confirm its part in promoting the manufacture of potash in America by offering premiums to British importers. An interesting illustration and one closely related to the work by Lewis can be seen in a letter written in 1766 from a member of the Society, Jno. [John] Mascarene of Cambridge, New England. This throws light on contemporary thinking regarding the status of potash manufacture, its supply, and the dearth of analytical knowledge. Mascarene had been making potash for about twelve years and in referring to exports of this material to England he mentioned concern about its quality (7):

But as all advantages are liable to abuse, and we have good reason to believe that a considerable quantity of Pot-Ash has been exported within this Year or two from thence to the English market, which was found not only bad in quality, but some Casks filled with an heterogeneous mixture.

Adulteration of the potash is obviously suspected, and he requests information regarding the lowest acceptable quality and the method of determining this. Lewis's use of a titrimetric method and color indicator to determine alkali content in American potashes shows a marked advance over earlier analytical methods. For example, in 1729 C. J. Geoffroy, in an essay presented to the French Academy and later published (8) in *Mémoires de l'Académie Royale des Sciences* (Paris, 1731), described an analytical method to determine the strength of vinegar by adding a controlled amount of powdered potassium carbonate to a known amount of vinegar until effervescence ceased. By this method Geoffroy formed a comparative idea of the vinegar's strength from the amount of potash used. Clearly this was an example of the quantitative use of an acid base reaction and employed aspects of what we now term titrimetry. However, the end point, or the point of "full saturation," can only have been within the observable accuracy given by cessation of effervescence.

This early record of an analytical process involving neutralization between an acid and a base occurred 27 years before the publication of Francis Home's *Experiments on Bleaching* (1756). Home's method of determining the strength of various alkaline salts such as pearl and blue ashes depended upon the use of a teaspoon as a volumetric measure (9):

In order to discover what effect acids would have on these ashes, and what quantity of the former the latter would destroy; from which I might be able to form some judgement of the quantity and strength of the salt they contained; I took a drachm of blue pearl ashes, and poured on it a mixture of one part spirit of nitre, and six parts water; which I shall always afterwards use, and call the *acid mixture*. An effervescence arose, and, before it was finished, 12 tea-spoonfuls of the mixture were required. This effervescence with each spoonful of the acid mixture was violent, but did not last long.

This was Home's method of measuring the strength of the alkali salt by neutralizing a weighed amount with a measured quantity of acid, the end point being the cessation of effervescence.

Lewis's original report on his work on American potashes is held by the Royal Society of Arts; the title page of the printed transcription reads (10):

*Experiments and Observations on American Potashes with An easy Method of determining their respective Qualities. By W. Lewis, M. B. F.R.S. Made at the Request of the Society for the Encouragement of Arts, Manufactures, and Commerce, in consequence of an Application from the House of Representatives of Massachusetts Bay. Printed by order of the Society, 1767.*

Eight potash samples were submitted to Lewis by the Society, and his report begins with a detailed comment on their physical appearance, taste, etc., and the wide variation of solubility in water. Using four-ounce samples, he determined the total dissolved solids in the clear filtrates by complete evaporation. After drying the crystals at "a moderate heat, below red hot," he showed by weighing that all eight samples contained over three ounces of soluble salt. Quantitative recrystallizations were carried out in an attempt to separate any salts present other than the alkali (potash). Lewis easily identified the initial nonalkali crystals, since in his experience true alkali would not crystallize out at the chosen dilution. Thus vitriolated tartar (potassium sulphate) and sea salt were isolated and a dried mixture of these, when tasted, indicated their presence together with some alkali; such was the application and apparent sensitivity

of tasting in this period. However, later in the report Lewis showed little enthusiasm for this method based on crystallization (11):

[this] was found so difficult and tedious, that the enquiry was dropt, and another way of examination tried.

That other way was to be:

...the quantity of true alcali in the salts might be discovered by their power of saturating acids, compared with that of an alcali of known purity; and this method succeeded so well, that it is hereafter proposed for the assaying of Potashes, and the manner of procedure described at large.

Tabulation of Lewis's results of the eight samples showed marked variation in alkali content. In this 34-page publication he described his analytical procedures in only the last four pages; and it is these that are now to be considered. In the opening paragraph he referred to other chemists who, using the methods now being considered, only achieved comparative results and not absolute values. In order to achieve accuracy he emphasized certain technical details; for example, he realized that the presence of 'earthy matter' in the potash samples would affect the amount of acid needed for complete saturation; this, and any other impurities must therefore be removed before the determination. As mentioned above, he dissolved the soluble or true alkali in water and removed any insoluble earthy material by filtration. He made no claim for the originality of this procedure which certainly became a standard technique (12):

The quantity of acid, necessary for the saturation of the lye, should be determined, not by drops or teaspoonfuls, but by weight [*a clear reference to Home's work*]; and the point of saturation, not by the ceasing of the effervescence, which it is extremely difficult, if not impracticable, to hit with tolerable exactness, but by some effect less ambiguous and more strongly marked, such as the change of colour produced in certain vegetable juices, or on paper stained with them.

In acknowledgment of Lewis's early use of a chemical indicator, it seems appropriate to quote his further instructions on this topic (13):

The finer sort of purplish blue paper used for wrapping sugar in, answers sufficiently well for this purpose; its colour being changed red by slight acids, and afterwards blue or purple again by slight alcalies. What I have chiefly made use of, and found very convenient, is a thick writing paper stained blue on one side with an infusion of lacmus or blue archil, and red on the other by a mixture of the same infusion with so much dilute spirit of salt as is sufficient

just to redden it. The paper is washed over with a brush dipt in the respective liquors, two or three times, being dried each time, till it has received a pretty full colour, and afterwards cut in slips a quarter of an inch or less in breadth; a bit of the end of one of the slips being dipt in the liquor to be tried, the red side turns blue while any of the alcali remains unsaturated, and the blue side turns red when the acid begins to prevail. If either the acid or alcali considerably prevails, the paper changes its colour immediately on touching the liquor: if they prevail but in a low degree, the change is less sudden. The part dipt is always to be cut off before a fresh trial.

Lewis chose spirit of salt (hydrochloric acid) rather than sulfuric acid in his belief that hydrochloric acid would not react with any sodium chloride that might be present in the soluble portion of the potashes under test. He gave very precise instructions on the method of preparing a conveniently diluted acid solution and of standardizing it by using a carefully weighed amount of perfectly dry potassium carbonate (Lewis assumed 100% purity). At no point did he know the actual amount of hydrochloric acid in his 'standard' dilute solution; this was not important for he was not calculating, as we would today, the results of a chemical reaction based on a chemical equation involving molecular weights as units in the calculation. What is significant in these details is that he standardized the acid by giving it a numerical value of strength in terms of equivalence to a known weight of what he believed was pure potash. Once this had been established, aliquots of the same acid could be used in subsequent determinations.

It would have been difficult to achieve greater accuracy in measuring the amount of acid used in the titration by any method other than that advocated by Lewis. In this simple gravimetric technique, a vial of dilute acid was merely counterpoised on a balance (there is no mention of its sensitivity). After he had poured off the amount needed for complete saturation of the potash, he again counterpoised the vial. The weight difference indicated the amount of acid used. Lewis extended this further by using a fixed amount of sample, whereby he could read directly the amount of potash from the marked balance weights.

It would be an exaggeration to claim that Lewis introduced the idea of what became known as "back titration" but he hints that if the end point, the change in color of the indicator, is accidentally exceeded, it is not necessary to repeat the entire experiment. This can only be taken to mean that more alkali might be added and the true end point determined more carefully. Then it

would follow that the net amount of base for neutralization be recalculated accordingly.

Regarding the possible presence of causticity (hydroxide), Lewis offered the following observation (14):

A person accustomed a little to this operation [*the titration*], will be able to determine by it, not only the quantity of pure alcali, but whether the alcali has any injurious causticity. Plain alcalies effervesce with the acid, from almost the first drop, till the saturation is completed: those which are fully caustic, make no effervescence at all; and those which are caustic in part, do not begin to effervesce, till a considerable quantity of the acid has been added, more or less according to the degree of causticity.

Within this original report Lewis included a section entitled "Hydrostatic assay of the strength of lyes, and of the quantity of saline matter contained in Potashes (15)." In order to determine accurately the density of lyes he devised an improved hydrometer, which gave a direct reading of the weight of potash in a pound of lye. He also recognized the importance of temperature in 'hydrostatic assays' but, more importantly, the limitations of the method (16):

To determine whether this salt be the pure alcali which it ought to be, recourse must be had to operations of a different kind, such as that described in the following article.

Here follows Lewis's titrimetric method.

Lewis's acid-base titration contains features and principles, for which there are apparently no precedents. His account of what now may seem to be a simple titration must stand as one of original invention marking a very important and well authenticated advance in early titrimetry. At no time did Lewis allow anything less than perfectly measured volume; also, he often resorted to measures of weight in order to reinforce perfectly acceptable volumetric measurement. However this aspect alone hardly stands as one of invention, and neither does his use of colored indicators; but taken together and with his rejection of the cessation of liberated carbon dioxide as a reliable end point, we see Lewis's work as an achievement of significance. The suggestion to use hydrochloric acid and not sulphuric is interesting inasmuch as Lewis anticipated a reaction between the latter and soluble marine salt (NaCl) in the potash solution; but the validity of this point is unimportant when compared with the meticulous procedure he used in preparing the acid solution and the potassium carbonate for the standardization process (17):

Take a quantity of spirit of salt [*hydrochloric acid*], and dilute it with ten or twelve times its measure of water; fill with this mixture a vial that will hold somewhat more than four ounces of water: the vial which I find most commodious is nearly of the shape of an egg, with a broad foot that it may stand sure, a funnel-shaped mouth for the convenience of pouring the liquor into it, and a kind of lip or channel at one side of the mouth, that the liquor may be poured or dropt out without danger of any drops running down on the outside. Hook the vial, by means of a piece of brass wire tied round its neck, to one of the scales of a balance; and counterpoise it, while filled with the acid liquor, by a weight in the opposite scale.

Although this does not describe a modern buret or measuring cylinder, the results would probably have been very accurate, provided the balance was sufficiently sensitive. It was this dilute acid solution which Lewis would titrate against one eighth of an ounce of prepared pure potash. This was made from thoroughly dried salt of tartar (potash, presumably from recrystallized material) followed by fusion, and then taken up in "an ounce or two of water." His description of this standardizing titration follows (18):

Pour gradually some of the acid from the vial into the solution of salt of tartar, so long as it continues to raise a strong effervescence; then pour or drop in the acid very cautiously, and after every small addition, stir the mixture well with a glass cane, and examine it with the stained papers. So long as it turns the red side of the paper blue, more acid is wanted: if it turns the blue side red, the acid has been overdosed. That there may be means of remedying any accident of this kind, without being obliged to repeat the whole preceding part of the experiment, it will be proper to reserve a little of the alkaline solution in another vial: this is always to be added towards the end, and washed out of the vial with a little water.

When the liquor appears completely saturated, making no change in the colour of the paper, hook the vial on the scale again, to see how much it wants of its first weight: this deficiency will be the quantity of the acid liquor consumed in saturating the two drams of alkaline salt. So much as this quantity wants of four ounces, so much, in proportion, of common water must be added to all the rest of the acid mixture. If for instance the quantity consumed in the saturation is three ounces, then, for every three ounces, or three pounds, or thirty pounds, of the acid liquor, must be added one ounce, or one pound, or ten pounds of water; the acid will thus be so adjusted, that four ounces of it will saturate two drams [*one eighth of an ounce, assuming Avoirdupois*] of alcali: it will be expedient to make another trial, to see whether it is exactly of this strength.

Put more simply, Lewis had shown that four ounces of his standard hydrochloric acid of unknown strength would always saturate one eighth of an ounce of pure potassium carbonate; in other words, he had standardized the acid against pure potassium carbonate. This was a unique feature and a significant practical achievement of that time, for in so doing, he demonstrated the way in which an absolute quantity could be determined. Madsen (19) has calculated the acid concentration expressed as HCl as 1.6 - 1.7% or 0.4 - 0.5 molar, but little useful historical value can be drawn from such a present day recalculation.

Speed and simplicity, characteristics of titrimetry, are illustrated in Lewis's developments. They may not have been essential requirements in his time, but no doubt became so, as the application of the procedure became useful in other industrial processes. In preparing and standardizing the acid within the range quoted above, Lewis arrived at a final calculation of marked simplicity; the weight of acid consumed, multiplied by four, indicated the quantity of pure alkaline salt contained in every pound of original sample. Within these six pages of reporting, Lewis had described all the essential practical features of what is now recognized as acidimetric titration. His report reflects an exceptional piece of analytical development. His rejection of approximate volume measurement in favor of weighing, the use of color to provide clear evidence of the completion of reaction, the creation of a standardized solution (albeit, not one based on molecular weight) all led to a method of determining absolute content, provided of course that his "pure" potassium carbonate was actually pure.

Lewis's titrimetric work was published in 1767 and, as already noted, it contained a definite, if indirect, reference to Francis Home's *Experiments on Bleaching* of 1756 (20). In determining the quality of American potashes by using a colored indicator, the standardization of the acid and the extreme accuracy in measuring and weighing, Lewis was significantly in advance of earlier methods particularly that suggested by Home in 1756. These improvements in titration taken together with his earlier analyses of Virginian Saltpetre (21), in which he emphasized the value of obtaining concordant analytical results and comparison against known standards, place Lewis's work of extreme importance in the development of early titrimetric analysis.

Oddly, in both pieces of work Lewis made no mention of moisture content in the original sample material, and there appeared to be some uncertainty about water

of crystallization. The latter was certainly not entirely understood at this time although Lewis had given some account of this in *Philosophical Commerce of Arts*, four years earlier. It is surprising therefore that occluded moisture in such commercial and impure products as saltpetre and potash had no consideration. Nevertheless, his awareness of what he believed to be absolute values of content must be noted as a major advance in the early stages of titrimetry.

His earlier work on Virginian Saltpetre involved the determination of the strength of nitric acid, but he saw this as merely balancing acid against alkali in terms of "saturation." However, his later experiments on potash show a distinct belief in true chemical content in absolute values; of course, we may now interpret this differently inasmuch as he was without the modern foundations of chemical formulae, equations, and molecular weights which we now see as essential in analysis.

It is surprising that there was so little recognition given to Lewis by several Scottish chemists in their later attempts to determine the alkali content in such materials as potash, ashes, kelp, and barilla. Fyfe, Jameson, and even Kirwan *et al.* were seemingly trying to reinvent the work already done by Lewis even though his innovative progress in titrimetry had been published by the Society of Arts. The explanation for this is not immediately obvious. Madsen commented (22):

It is strange that the analytical part of this treatise was not at all understood by Lewis's contemporaries, and that the treatise does not seem to have left any mark in the development of analysis.

The same enigma was described by Gibbs (23):

He [Lewis] was celebrated as a physician and occupied a secure place as the foremost British pharmaceutical writer of his day; his books were widely used, in particular by Cullen and Black at Edinburgh. Yet apart from a few scattered references to him in the literature of pharmacy, one can search the histories of the special sciences in vain for an indication of the extent of his work....Lewis was one of the best known and least known scientists of his period.

It is difficult to determine the audience reached by this early analytical work; Lewis's 1767 paper was published in London and copies were sent to the Colonies, but it is surprising that his analytical achievements were not better appreciated outside the interests of the Society of Arts (24).

This short account of Lewis's writings and analytical developments clearly shows his concern for the improvement of 'the arts.' His work on the analysis of

potashes and other researches on their manufacture were in the context of the promotion by the Society of Arts to import these materials from British Colonies rather than from uncertain European sources. In this work he did not aim solely at a theoretical understanding of chemical processes like that, for example, offered by Joseph Black (25). The latter saw chemical understanding of early bleaching of raw materials as a means of immediate help to bleachers, but in fact this was not borne out in practice for their rule-of-thumb empirical methods continued. Lewis attempted to show that chemical analysis could be used to improve 'the arts' by providing accurate means of determining quality and hence value and suitability to the user.

Lewis undoubtedly led the field in showing that practical chemistry through analysis could provide answers to industrial questions. His analytical work and hydrometry researches, alone, place him supreme for the period. His main texts, *Commercium Philosophico-Technicum* and *Chemical Works of Caspar Neumann* are full of answers to manufacturing problems and possibly set a pattern for future authors in this field. The researches on platinum were extensive and represented a program of work that proved the metallic status of platinum and its chemical detection as an adulterant of gold (26). As a quantitative chemical experimentalist his work on American potashes clearly exemplified the future alliance between science and industry.

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After retiring from the chemical industry in 1989, the author pursued an interest in history of science and gained an M.Sc., at the Oliver Lodge Laboratory of the University of Liverpool. His studies of early industrial analytical chemistry under the supervision of Professor W. H. Brock resulted in his earning a doctorate from the University of Leicester in 1999. The above article is a condensed and modified extract from his thesis.

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