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ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON ANALYTICAL NOMENCLATURE

in conjunction with

THE SOCIETY FOR ANALYTICAL CHEMISTRY
ANALYTICAL METHODS COMMITTEE

SODIUM CARBONATE AND
SULPHAMIC ACID AS
ACID-BASE PRIMARY STANDARDS

LONDON
BUTTERWORTHS

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INTRODUCTION

At the I.U.P.A.C. Conference held in Munich during 1959, the Committee of the Division of Analytical Chemistry was asked to recommend suitable primary standards for acid-base titrimetry. The Committee, after some discussion, concluded that it was a matter which should first be examined at national level, owing to the widely different views reported in the literature.

Professor R. Belcher (U.K.), at that time President of the Division, was asked to propose to the Analytical Methods Committee (AMC) of the Society for Analytical Chemistry, that it might undertake this examination; Commission V.3. was allotted the duty of effecting liaison in the event of the AMC accepting the proposal.

The AMC agreed to undertake this examination and appointed a sub-committee, under the Chairmanship of Mr. E. Bishop, to investigate in detail the reliability of selected established standards and of certain "newer" standards, on which an independent assessment was not available. Lists were prepared of the two categories of standard.

As a result of this investigation, two standards, one alkaline¹ and one acidic², have been recommended. An examination of the properties of other acid-base standards which have been proposed, is in progress.

The Division of Analytical Chemistry has approved both reports and recommends these two compounds, sodium carbonate and sulphamic acid as International Primary Standards.

The Division takes this opportunity of thanking the AMC for undertaking these exhaustive and thorough studies on their behalf.

CLASSIFICATION OF STANDARDS

The following grades of standard were defined for application to the present and future work:

- A. Reference or atomic-weight standard (e.g. atomic-weight silver).
- B. Ultimate standard; a substance that can be purified to virtually atomic-weight standard.
- C. Primary standard; a commercially available substance of purity 100 ± 0.02 per cent.

- D. Working standard; a commercially available substance of purity 100 ± 0.05 per cent.
- E. Secondary standard; a substance of lower purity that can be standardised against a primary standard.

SURVEY OF THE LITERATURE ON PROPOSED PRIMARY STANDARDS

From a critical survey of proposed primary standards not one emerged with an outstanding claim to first consideration, but sodium carbonate and sodium tetraborate decahydrate appeared to be the most promising.

Sodium carbonate can be obtained in a pure state, but some doubt exists about the precision of results obtained by its use, which involves the liberation of carbon dioxide. It is also necessary to dry it before use, and it may be hygroscopic. Sodium tetraborate can also be obtained in a pure state, but has the disadvantage of being hydrated, thereby necessitating storage in a hygrostat.

Several acids were considered. Potassium hydrogen phthalate is probably not commercially available with a purity of better than 100 ± 0.05 per cent, and is limited in its application by its low second ionisation constant. Different opinions are held on the method of preparation and the purity of sulphamic acid, but it was considered that the purity of the commercially available material was about 100 ± 0.05 per cent. Further, it was thought that it was theoretically disadvantageous to use a material that decomposes in solution, even though its titre remains the same. Potassium bi-iodate is a stable non-hygroscopic substance; it has a high equivalent weight and is bi-functional. However, some doubt exists about its stoichiometry and its purity is regarded as being only 100 ± 0.05 per cent. Benzoic acid is undoubtedly available in a highly pure state, but it has the disadvantage of being a weak acid that is not particularly soluble in water.

As little published information was available on the other substances included in the survey it was realised that further work would be necessary before a true assessment of their value could be made. It was decided that, as no definite evidence was available showing that any one of these substances was more promising than sodium carbonate or sodium tetraborate, no collaborative investigation of these other substances would be undertaken at this stage.

Of the substances considered to be the most promising, work was begun on sodium carbonate and sulphamic acid.

SODIUM CARBONATE

In this Report a brief account of the various stages of the work and of the conclusions reached are given. The experimental procedures used in the assays require facilities and conditions not commonly available in many laboratories.

Assay of sodium carbonate

Two possible methods for the high-precision assay of sodium carbonate were considered, one involving relation to atomic-weight standard silver

through titration against hydrochloric acid and the other involving titration against benzoic acid. Both methods were suitable, both were used, and detailed procedures were drawn up. The titrations were of the partial neutralisation type to alleviate the difficulties of carbon dioxide removal; for the titration against hydrochloric acid, 50 ml of 1.0 M hydrochloric acid were dispensed from a weight burette and allowed to react with 99.8 per cent, of the theoretical amount of sodium carbonate. The titration of the 0.2 per cent excess of hydrochloric acid was completed with 0.05 M barium hydroxide, itself standardised against the hydrochloric acid. The hydrochloric acid was standardised against the silver. For the titration against benzoic acid, 2.5 g of sodium carbonate were neutralised with a 0.25 per cent excess of benzoic acid and the titration was completed with 0.05 M barium hydroxide, itself standardised against the benzoic acid.

For the collaborative assays carried out by these methods, common samples of zone-refined benzoic acid and of 1.0 M hydrochloric acid were used.

Assay against benzoic acid

Before beginning collaborative assays, some preliminary tests were done on stock materials by the proposed method. Immediately, some evidence of loss of benzoic acid during removal of carbon dioxide became apparent. An investigation showed this loss to be about 2 mg per hour at 60°C in a stream of nitrogen, and it was decided at this stage to make no further use of the assay against benzoic acid.

Later, when satisfactory results had been obtained by the assay against hydrochloric acid, interest in the benzoic acid method was revived. Modifications aimed at avoiding the loss of benzoic acid were introduced and the method was used to check the purity of samples of sodium carbonate already assayed against hydrochloric acid. However, evidence of loss of benzoic acid was still encountered, and an investigation of the loss confirmed the earlier findings; further, the spread of results for the assay of sodium carbonate was several times greater than that by the hydrochloric acid method. It was concluded that, although the purity of benzoic acid was not in doubt, the difficulties encountered in its use were too great for complete reliance to be placed on the results obtained, and the method was, therefore, abandoned.

Assay against hydrochloric acid

Standardisation of the hydrochloric acid. Nominally 1.0 M hydrochloric acid was prepared from constant-boiling hydrochloric acid and its concentration checked by reference to silver³. The silver was of "five nines" grade, and analysis revealed gas contents of 25 p.p.m. (by weight) of oxygen in the untreated silver (28, 35 and 30 p.p.m. in the treated material), 2 p.p.m. of hydrogen and 10 p.p.m. of nitrogen.

Collaborative assays. As no inherent difficulties were experienced in trials of the method, a series of collaborative assays was planned. Four samples of sodium carbonate (two from each of two sources) were distributed and the assays were carried out against hydrochloric acid prepared and standardised in each laboratory. To obtain the maximal information from as few assays as possible, a Latin Square was designed, and the results, when

inserted in this square, indicated a significant high bias in the results from one laboratory.

A further series of assays was carried out on four new samples (two from each of the same two sources) and the Latin Square appraisal was again used. Good agreement within samples was obtained, but the results indicated that approximately 0.04 per cent of the samples was unaccounted for in the assay. Examination with a medium-quartz spectrograph and copper electrodes indicated the presence in the two samples from one source of calcium (0.012 and 0.016 per cent) and silicon (0.002 and 0.003 per cent); no other impurities were detected. The samples from the other source gave on examination 0.014 per cent of calcium and evidence of the presence of potassium and aluminium. As it was possible that occluded water could make up the difference, it was decided to test for water by nuclear magnetic resonance spectroscopy; the technique, however, proved to be insufficiently sensitive for use at this level.

It was concluded that materials from the two sources so far examined did not meet the purity requirements of a primary standard.

Examination of sodium carbonate from a further commercial source

Spectrographic examination of a sample of sodium carbonate from a further commercial source had indicated only one faint line, which might have been due to aluminium. This sample, which was more than 25 years old, had a different physical appearance from the earlier samples tested, being in the form of free-flowing fine granules whereas the others had all been powders.

Two further samples of sodium carbonate from different batches were obtained from this further commercial source and collaborative assays on all three samples were carried out in four laboratories. In all, results of 33 assays all within the range of 99.80 to 100.010 per cent, the mean being 99.993 per cent with a standard deviation of ± 0.005 .

It was apparent that sodium carbonate from this commercial source met the requirements of a primary standard. Not all commercial sources of sodium carbonate had been investigated, but a programme of work involving an investigation of this magnitude was considered impracticable. However, it was considered that it could be stated with confidence that sodium carbonate suitable for use as a primary standard was available commercially.

Laboratory preparation of primary standard grade sodium carbonate

After the work on commercially available sodium carbonate had been completed, it was decided that sodium carbonate satisfying the requirements of a primary standard might be prepared in the laboratory by a method involving ignition of analytical-reagent grade sodium hydrogen carbonate that had been recrystallised from water. Full details of the method of preparation are given in Appendix I.

Two samples of sodium carbonate were prepared by this method in two laboratories and were assayed on a collaborative basis. The results of 13

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assays, which were all within the range 99.985 to 100.01 per cent, had a mean of 99.996 per cent with a standard deviation of ± 0.008 .

The results indicate that sodium carbonate prepared by the method described in Appendix I meets the requirements for a primary standard.

Conclusions

As a result of the collaborative work extending over four years that is described in this report, it is recommended that sodium carbonate is a suitable substance for use as a primary standard. Further, it is known that there exists at least one commercial source of sodium carbonate that is within the required assay limits for a primary standard, and that sodium carbonate prepared as described in Appendix I is also satisfactory.

The standard deviations on the results of the two final assays indicate that the analytical procedure used affords a certainty of better than 0.01 per cent, and is well within the requirements for materials of primary standard grade.

SULPHAMIC ACID

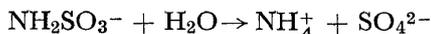
Sulphamic acid has previously been recommended for use as a standard in acid-base titrimetry by Butler, Smith and Audrieth⁴.

Suitability of sulphamic acid for use as a primary acidimetric standard

Before collaborative assays of sulphamic acid began, the following aspects of its general suitability for use as a primary standard were investigated in one laboratory.

Hygroscopicity. Ten grams of specially purified sulphamic acid that had been dried for 4 hours *in vacuo* over concentrated sulphuric acid were weighed into a shallow glass dish of base area 45 cm². The acid was pressed down with the bottom of a beaker to give a flat and even surface over the entire base area of the dish. Except during weighing, the dish was covered with a large cover-glass, raised to allow free access to the atmosphere. The dish containing the acid was weighed at intervals over 6 hours and again after about 24 hours; at the same time wet- and dry-bulb thermometer readings close to the balance were recorded. Over the entire period a loss in weight of 0.00022 g was recorded and during this period the dry-bulb fluctuated between 21.9 and 22.0°C and the wet-bulb between 15.3 and 18.1°C. It was concluded from these observations that no special precautions would be needed in carrying out accurate weighings of the anhydrous acid in air.

Loss of sulphamic acid during boiling. In the method of assay that was proposed for subsequent work a slight excess of sulphamic acid is present in solution while boiling out carbon dioxide. As sulphamic acid is known to hydrolyse in boiling water in accordance with the equation



it was necessary to know whether or not this reaction would affect the subsequent titre. Two identical solutions were titrated with 1.0 M sodium hydroxide, one in the cold, the other after having been boiled for 5 minutes and

then cooled; the titres were 100.01 and 100.02 ml, respectively. After an assay, several successive increments of 3 to 22 mg of sulphamic acid were added to the neutralised solution, and each was titrated with the same standard alkali. The equivalent titres for the several increments were identical, whether or not the solution was boiled. Any loss or decomposition of sulphamic acid has, therefore, a negligible effect on the assay. Potentiometric titration of 10 mg of sulphamic acid and of ammonium hydrogen sulphate in 30 ml of water with 10^{-3} M alkali showed that the end-point pH in the latter instance was 0.2 pH less than for sulphamic acid.

Thermal stability of sulphamic acid. The thermal stability of sulphamic acid was investigated both by heating on a thermobalance and by prolonged heating in an oven at 106°C.

Two sets of experiments were carried out. In the first set, the sulphamic acid was heated in a dry, carbon dioxide-free atmosphere of argon in an oven at 106°C for 18 days and on a thermobalance from ambient temperature to 300°C. When heated in the oven, the sample was unchanged, but on the thermobalance, decomposition began at about 140°C, leading to the formation of diammonium imidodisulphonate, $\text{NH}(\text{NH}_4\text{SO}_3)_2$ (identified by x-ray diffraction), which was unchanged up to 300°C, although there was evidence of slight volatilisation at this temperature.

In the second set of experiments, air was used in place of argon and no precautions were taken to exclude moisture. Under these conditions, when the sample was heated in an oven at 100°C for 18 days, a slow increase in weight was observed and the final product was shown to be ammonium hydrogen sulphate. When heated on the thermobalance, a gain in weight was observed after 1 hour at 136°C and, after 6 hours at this temperature, the rate of weight increase was about 10 mg per hour; after about 50 hours no further gain or loss in weight was recorded. X-ray diffraction examination of a portion of the product showed that the only crystalline phase present was ammonium hydrogen sulphate. The product was subjected to higher temperatures, and, at 310°C, began to lose weight at a constant rate. The presence of both ammonium hydrogen sulphate and ammonium pyrosulphate in the product was indicated by x-ray diffraction. At 400°C and above, decomposition of the sample took place rapidly.

From these experiments it was concluded that the sulphamic acid decomposes rapidly at temperatures above 136°C and that this decomposition may proceed more slowly at lower temperatures. Further, any moisture in the sample or in the surrounding air will react at 100°C with sulphamic acid, producing ammonium hydrogen sulphate by hydrolysis. Therefore, it is recommended that sulphamic acid be dried by standing *in vacuo* over a suitable desiccant such as phosphorus pentoxide.

Assay of sulphamic acid

The high precision method of assay adopted for use in this work was provided by one of the collaborating laboratories. Essentially, the method consists of adding to a solution containing a known weight of primary-standard grade sodium carbonate, 3 to 5 mg more sulphamic acid than the theoretical amount necessary for neutralisation of the sodium carbonate.

The sodium carbonate was previously assayed against ultimate standard silver. The carbon dioxide generated is removed by boiling and the excess of sulphamic acid is titrated in a carbon dioxide-free atmosphere with 0.01 M sodium hydroxide.

Collaborative assays

In work on sodium carbonate¹, commercial sources of the material were investigated before undertaking work on laboratory-purified samples. When the present work was begun there was no knowledge of commercial sources of sulphamic acid that could confidently be relied upon consistently to meet the requirements for a primary standard, although a well-known source of certificated material exists. Samples of sulphamic acid from this source have been examined and the results of three assays were 99.94, 99.97 and 99.96 per cent. It was decided, therefore, that the initial work should be undertaken on a sample of sulphamic acid purified some years previously by one of the collaborating laboratories. A common sample of primary standard sodium carbonate was circulated for use in the assays.

Preliminary assays to acquaint the members with the assay procedure were carried out, and the method was reported to be free from inherent difficulties. Some differences of interpretation of the manipulative details did, however, cause some collaborators to return erratic results during the preliminary work, but these differences were soon resolved.

In the subsequent collaborative assays of the specially purified batch of sulphamic acid against a single sample of primary standard sodium carbonate (purity 100.00 per cent), the mean of 26 results obtained in four laboratories was 100.0005 per cent, with a standard deviation of ± 0.009 . All of the results were within the range 99.98 to 100.02 per cent².

Laboratory preparation of primary standard sulphamic acid

To demonstrate the reproducibility of the purification procedure used to prepare the single satisfactory sample of sulphamic acid, the laboratory that produced this sample undertook to purify a further batch. Two other collaborators also undertook to follow the same purification procedure and prepare batches of the material. As the stock of sodium carbonate used in the previous assays had been exhausted, a further batch for use in subsequent assays was prepared by the method described in Appendix I.

The three batches of purified sulphamic acid were assayed in four laboratories and two of them were found to be satisfactory. The third batch, prepared by one of the two collaborators with no previous experience of the purification procedure, was found to be unsatisfactory. On examination, this sample was found to differ in appearance from the satisfactory batches in that its crystal size was more variable. This laboratory has also recorded a considerably larger yield from the purification procedure than had the other laboratories. Two further unsuccessful attempts were made to purify batches of the material, and on both occasions comparatively high yields were obtained and the distribution of crystal sizes in the final product was variable.

In an attempt to resolve the difficulties being experienced in this one

laboratory, a detailed investigation of the purification procedure was undertaken in the laboratory from which it originated. At the same time further satisfactory batches of sulphamic acid were prepared in this laboratory, one of them by a worker with no previous experience of the procedure.

It appeared, therefore, that it was the factors governing the magnitude of the yield from the purification procedure that were of primary significance, as illustrated in *Table 1*, and not the purity of the starting material. The purification procedure was therefore re-written in considerable detail with particular attention to the temperatures and approximate durations of each stage, and to the washing of the final product. It has been concluded that the critical factors are as follows: (a) it is essential that the temperature range and rate of cooling in the production of the final crop of crystals, selected to minimise hydrolysis, produce a small particle size and maintain a fast separation rate, (b) the washing procedure, again designed to minimise hydrolysis, must remove contamination of the crystals quickly and expel the water as quickly as possible. When the unsatisfactory batches mentioned above were bulked dry and carefully re-washed, the product assayed well within the required limits.

Table 1. Effect on purity of the yield from the purification procedure

<i>Batch No.</i>	<i>Sulphamic acid (%)</i>		<i>Yield (%)</i>
	<i>Before purification</i>	<i>After purification</i>	
1	99.2	100.001	21.6
2	99.2	99.994	24.5
3	99.5	99.997	24.2
4	99.5	99.987	26.8

Two further batches of sulphamic acid were then purified, one by the collaborator who had previously been unable to produce a satisfactory product, and the other by a fourth laboratory that had not previously participated in the practical aspects of the work. No difficulties in following the detailed procedure were experienced in either laboratory and both batches assayed well within the specified limits of purity for a primary standard.

Full details of the recommended procedure for purifying sulphamic acid, which is a modified version of the method proposed by Butler, Smith and Audrieth⁴ are given in Appendix II. As the method of Butler, Smith and Audrieth was reported to give a product assaying as 99.5 per cent pure and required the rejection of the first three crops of crystals, a simple extension to the rejection of four top crops was adopted, as well as the clarification of detail. Although this method gives a satisfactory product, no investigation of the effect of reducing the number of top croppings, while maintaining the temperature range of the final cropping, has been made, apart from one observation that a single top crop did not give a satisfactory product.

Finally, four batches of material prepared by the modified procedure by four separate laboratories were subjected to collaborative assay; the results are shown in *Table 2*.

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Table 2. Collaborative assays of laboratory-purified sulphamic acid

Laboratory	Sample prepared by laboratory			
	A	B	C	D
A	99.994	99.995	99.999	99.991
B	99.999	99.99	100.01	10.00
C	100.002	99.999	99.995	100.000
	Mean	99.998	
	Standard deviation	±0.005	

Conclusions

As a result of the collaborative work described in this report, it is recommended that sulphamic acid is suitable for use as a primary standard. However, at present there appears to be no commercial source of the acid that can be expected to assay consistently within the acceptable limits for a primary standard.

Sulphamic acid purified in accordance with the procedure described in Appendix II will assay within the prescribed limits, and is suitable, therefore for use as a primary standard.

APPENDIX I

LABORATORY PREPARATION OF PRIMARY STANDARD SODIUM CARBONATE

Starting material

Sodium hydrogen carbonate : Analytical-reagent grade.

Procedure

Add gradually, and with frequent stirring, 769 g of the sodium hydrogen carbonate to 3 litres of distilled water at $86^{\circ} \pm 1^{\circ}\text{C}$ in a hard-glass 4-litre beaker. Maintain the solution at this temperature until all the solid has been added and has dissolved. Remove the beaker from the source of heat and stir the solution until the temperature falls to 75°C and a small crop of crystals has precipitated. Pass the solution, without further cooling, under suction through a close-grained filter-paper supported on a previously warmed large Buchner funnel. Cool the filtrate quickly and with stirring until the temperature falls to 18° to 20°C and the main crop of crystals is separated. Collect the crystals on a Whatman No. 541 filter-paper supported on a Büchner funnel, and remove as much as possible of the mother liquor by suction. Wash the crystals on the filter-paper once with a small amount of ice-cold distilled water, and dry them as completely as possible under suction. Transfer the damp crystals to a porcelain basin and dry them by heating at 100°C ; stir the mass from time to time during the drying. Lightly grind the dried crystals to a powder, mix the powder thoroughly and convert it to sodium carbonate by heating to constant weight at $270^{\circ} \pm 10^{\circ}\text{C}$ in a platinum basin.

APPENDIX II

LABORATORY PURIFICATION OF SULPHAMIC ACID

Starting material

Sulphamic acid: Commercial grade.

Apparatus

Filter flasks (2): Capacity 5 litres.

Safety cage: Suitable for use with 5-litre filter-flasks.

Büchner funnels, porcelain (2): Diameter 12.5 cm.

Filter-paper: Whatman No. 542, or equivalent, diameter 12.5 cm.

Beakers (2): Squat form, borosilicate glass, capacity 4 litres.

Sintered-glass funnels (2): Plate diameter 9 cm, porosity No. 3, capacity approximately 500 ml.

Procedure

Fit a 5-litre flask with a Büchner funnel supporting a 12.5 cm Whatman No. 542 filter-paper, and insert a suitable catch-pot between the flask and the source of suction.

Heat 3 litres of distilled water in a 4-litre beaker to 80°C on a hot-plate, remove the beaker from the hot-plate, and immediately add 1250 g of commercial-grade sulphamic acid, and stir vigorously for 2 minutes. Without delay, filter the solution through the prepared filter. There are occasions when the filter-paper becomes choked with fine crystals. When this occurs, filtration virtually stops, and it is advisable, therefore, to have a second Büchner funnel at hand, fitted with a No. 542 filter-paper. The choked filter can then quickly be replaced, any unfiltered solution in it transferred into the new filter and filtration continued with a minimum of delay. Discard the excess of sulphamic acid, together with visible impurities.

Allow the filtrate in the flask to cool until a small crop of crystals appears, and then pass the solution through a second filter prepared in the same manner as the first; again discard the material collected. At this stage an examination of the filter from the second filtration should indicate the complete removal of all visible impurities. For the next two filtrations the No. 542 filter-paper can be replaced by a more porous filter such as a No. 541 filter-paper, or by a No. 3 porosity sintered-glass funnel. Repeat these operations until the solution has been filtered four times, the crop of crystals produced being discarded on each occasion. Then decant the filtrate from any crystals that may have been deposited, into a clean 4-litre beaker. Stand the beaker in a bath of crushed ice-salt mixture until the temperature of the solution has fallen to between 20° and 21°C. (In cooling the solution, 20°C should be taken as the absolute minimum, and it is advisable to filter off the crop of crystals immediately before this temperature is reached.)

An example of the temperature recorded at the various stages during a purification is given below, and will serve as a rough guide to the temperature drops that can be expected.

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|-------|--|----|----|----|----|------|
| (i) | Water heated on hot-plate | .. | .. | .. | .. | 80°C |
| (ii) | Solid added and stirred for 2 minutes; temperature immediately before 1st filtration | .. | .. | .. | .. | 62°C |
| (iii) | Temperature immediately before 2nd filtration | .. | .. | .. | .. | 52°C |
| (iv) | Temperature immediately before 3rd filtration | .. | .. | .. | .. | 50°C |
| (v) | Temperature immediately before 4th filtration | .. | .. | .. | .. | 46°C |
| (vi) | Temperature immediately before cooling procedure | .. | .. | .. | .. | 42°C |
| (vii) | Temperature immediately before filtering off final product | .. | .. | .. | .. | 20°C |

The time required to carry out the complete procedure, from adding the solid to the water at 80°C to the end of the 30-minute aeration period, is about 2 hours.

Stir the solution vigorously during the cooling process (preferably with a mechanical stirrer) so as to produce small crystals. Remove the beaker from the cooling bath, carefully wash the outer surface to remove salt water, and dry it. Fit a sintered-glass funnel to a filter-flask, and connect to a source of suction. Remove the mother liquor by decantation, transfer the crystals of sulphamic acid into the funnel, and press down the crystals as firmly as possible to give an even surface. Apply the strongest suction attainable, which must be maintained during this operation and the subsequent washing procedures and allow the crystals to be sucked dry until all visible flow of mother liquor has ceased. This operation must be carried out with complete thoroughness; at least 5 minutes' suction must be applied after each wash.

From a small beaker pour 100 ml of ice-cold distilled water onto the crystals so that the entire surface is momentarily flooded. Allow the water to be removed by suction as completely as possible and then repeat the washing with a further 100 ml of ice-cold water. If the surface of the crystals has become disturbed, smooth out the mass and pack as firmly as possible.

In the same manner as described for the washing with water, wash the crystals twice with 100 ml portions of ice-cold absolute ethanol, twice with 100-ml portions of absolute ethanol at 20° to 25°C and, finally, with two 100-ml portions of anhydrous ether at 20° to 25°C. After the final wash, draw air through the mass for about 30 minutes to remove as much of the ether as possible. If this time is adhered to, it will be found that the crystals, on removal from the filter, are almost free from ether. It should be emphasised that each batch of crystals, after separation from the mother liquor, must be washed and dried in the manner described with a minimum of delay. Each batch must be treated separately, and on no account must batches be bulked together wet and then subjected to the washing and drying procedure. Transfer the crystals of pure sulphamic acid into a large porcelain basin or tray and dry for 4 hours in a well ventilated oven, thermostatically controlled at 60°C. Stir the mass frequently during this period. Allow the crystals to cool, and store the product in sealed hard-glass containers.

References

- ¹ Analytical Methods Committee, *Analyst*, **90**, 251 (1965).
- ² Analytical Methods Committee, *Analyst*, **92**, 587 (1967).
- ³ C. R. N. Strouts, H. N. Wilson and R. T. Parry-Jones, Editors, *Chemical Analysis, the Working Tools*. Clarendon Press, Oxford, 1962, Vol. I, p. 200 (see also *Analyst* **75**, 577 (1950)).
- ⁴ M. J. Butler, G. F. Smith and L. F. Audrieth *Ind. Eng. Chem., Anal. Ed.*, **10**, 690 (1938).