DETERMINATION OF AMMONIUM SULPHATE IN AMMONIA ALUM BY FORMALDEHYDE REACTION

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ABSTRACT

Existing methods for the estimation of ammonium salts in presence of hydrolysable salts have been reviewed. A new titrimetric method utilizing formaldehyde and potassium fluoride is described for its estimation in presence of aluminium sulphate. The method is accurate and rapid for routine analysis.

Introduction

Assessment of the purity of ammonium salts by titration of the acid obtained in a reaction of the type $6\ HCHO + 4NH_4Cl = (CH_2)_6\ N_4 + 4HCl + 6\ H_2O$ has been adopted as a standard method by Rosin Joseph[1] and Analar[2] standard. Aldo Rusconi[3] has advocated the use of 0·1% alcoholic solution of bromo-thymol blue in place of phenolphthalein used in the methods referred to above. Among other methods recommended for estimating ammonium salts alone or in admixture with other salts, mention may be made of the conventional distillation method and ammonia oxidation method[4 & 6]. However, experience shows that these methods require considerable skill and the results are vitiated due to the presence of ammonia vapour in a routine testing laboratory. Further, the conventional distillation method requires the use of costly ground glass equipment, the distillation flask of which very often needs replacement due to pores/cracks developed as a result of the action of strong caustic alkali solution and heat.

The present paper describes a method evolved in DRL(S), for the estimation of ammonium sulphate in ammonia alum by using formaldehyde in conjunction with potassium fluoride. The latter suppresses interference due to aluminium ions.

Experimental

Reagents required—Reagent grade chemicals and carbon dioxide free water were used except where otherwise stated.

1. Aluminium sulphate $(Al_2\,(SO_4)_3\,18H_2O)$ 5% (*w/v*) and 10% (*w/v*) aqueous solutions.
2. Ammonium sulphate $(NH_4)_2\,SO_4$ 1·0% (*w/v*) and 2·0% (*w/v*) aqueous solutions.
3. Ammonium aluminium sulphate $(NH_4)_2SO_4, Al_2\,(SO_4)_3, (24H_2O)$ 5% (*w/v*) solution.

4. Sulphuric acid :—0·1 *N* solution
0·5 N solution
5. Sodium hydroxide :—0·1 *N* solution
0·5 *N* solution
6. Formaldehyde :— 40·0% solution (Neutral)
7. Hexamine B.P.C. :— 20·0% (*w*/*v*) aqueous solution (Neutral)
8. Phenolphthalein :— 0·1% alcoholic solution
9. Thymolphthalein:— do.
10. Thymol blue (B.D.H.) :—As obtained from British Drug House Limited.
11. B.D.H. 9011 :— do.
12. Methylene blue :— 0·2% (aqueous solution)
13. Phenol red :— 0·1% (alcoholic solution)
14. Potassium fluoride :—B.D.H.L.R. 25% (w/v) K. F. (aqueous solution neutral).
15. Mixed indicator :—No. 1 A mixture of phenolphthalein, thymolphthalein & B.D.H. 9011 in equal proportions.

Procedure

(*a*) *Formaldehyde method—deferred titration*—The experimental work was divided into the following steps :—

(*i*) Determination of free acidity (i.e. blank titration) :—

Take 25 ml of 5% alum solution (freshly prepared and thoroughly mixed) in a polythene container or wax lined Erlenmeyer flask of about 250 ml capacity. Add 25 ml of potassium fluoride solution, 2 to 3 ml of mixed indicator No. 1 and titrate with 0·1 N standard alkali solution. Note the titre value.

(*ii*) Initial titration:—

Repeat the titration as at (*i*) above after adding 5 ml of formaldehyde solution prior to the addition of potassium fluoride solution. Note the titre value.

(*iii*) Deferred titration:—

Repeat titration as at (*ii*) above except that add potassium fluoride solution after 50% neutralisation of the liberated acid (calculated on initial titre value) and then complete the titration. Note the titre value.

Calculation—

Ammonium sulphate content (in g) $= (C - A) \times N \times 0{\cdot}06607$ where
C=ml of alkali solution required under step (*iii*)
A=ml of alkali solution required under step (*i*)
N=Normality of alkali solution.

(*b*) *Formaldehyde method—direct titration*—This involves two titrations as described under step (*i*) and (*ii*) above.

Calculation

Ammonium sulphate content (in g) = (B—A) × N × 0·06607 where

B=ml of alkali solution required under step (*ii*) above

A=ml of alkali solution required under step (*i*) above

N=Normality of alkali solution.

(*c*) *Distillation method*—The conventional ammonia distillation method was followed.

(*d*) *Expulsion method*—A modification of Kazumi Kondo ([7]) ammonia evaporation method was followed.

Take 25 ml of alum ammonia solution in an Erlenmeyer flask of about 250 ml capacity, add 50 ml of 0·5 N standard sodium hydroxide solution, boil for two hours replacing the water lost due to evaporation. Cool and transfer to a wax lined Erlenmeyer flask. Add phenolphthalein and titrate the excess alkali with 0·5 N sulphuric acid, after complexing aluminium with 25 ml of potassium fluoride solution.

Calculation

Ammonium sulphate content (in g) =[50—(E+D)] × 0·03304 where

E=ml of 0·5 N Sulphuric acid required for excess alkali.

D=ml of 0·5 N Alkali solution required for free acidity.

Results

Results on the comparative efficiency of the three methods under sub-para b, c & d of para 2 described above, are given in Table I & II, Table I containing the results obtained using a mixture of ammonium sulphate and aluminium sulphate in the proportions as found in alum ammonia [$Al_2(SO_4)_3$ $(NH_4)_2$ SO_4, $24H_2O$] while Table II giving the results obtained using alum ammonia.

Similarly the results derived from the application of formaldehyde method vide sub para 'a' of para 2 (deferred titration) are given in tables III & IV. The results on the potentiometric titrations carried out as per methods 'a' and 'b' are given in Fig. III.

Discussion of results

The results of table I & II confirm the accuracy of the conventional distillation method. It is also evident that formaldehyde method (direct titration) and ammonia expulsion method[7] give low results. Further, the results of the latter method are also not reproducible, even when the concentration of alkali added to expel ammonia was more than double the stiochiometric amounts required. This indicates that the conditions for arriving at accurate results with this method are rather critical.

The results obtained with the formaldehyde method 'b' (direct titration) although low are consistent and reproducible. Low recoveries are presumably due to the occlusion and or sorption of the acid (liberated from ammonium sulphate on addition of formaldehyde) by cryolite (formed in situ due to the addition of potassium fluoride). This is based on the work of Graham[5] and Amirchand[8] et al on the estimation of free acidity in aluminium sulphate and alum. These authors have shown that if addition of potassium fluoride is deferred then the error due to occlusion and or sorption can be avoided.

Stages of deferred addition of potassium fluoride for various concentrations of alum and mixture of ammonium sulphate and aluminium sulphate are given in Table III & IV. A perusal of the data shows that low or high acid recoveries result if potassium fluoride is added before or after the established deferred points. The former arises due to occlusion of acid and the latter due to the occlusion of $Al(OH)_3$ in cryolite. $Al(OH)_3$ is formed due to the hydrolysis of aluminium sulphate during the course of excess neutralisation of the acid beyond the established deferred addition point. An amount of acid corresponding to the amount of $Al(OH)_3$ occluded remains in solution, resulting in overall high acid recoveries.

The data given in Tables III & IV are plotted in Fig I. A study of the graph shows that for ammonium sulphate content of the alum ammonia ranging from 0·08 gm to 0·125 gm and from 0·2 gm to 1·0 gm the addition of potassium fluoride in the deferred titration should be made at 90% and 50% neutralisation of the liberated acid. In the intermediate range of 0·125 gm to 0·2 gm ammonium sulphate content, the point of deferred addition varies with its concentration. From the known initial titre values one can thus directly evaluate with the help of this curve, the point for the deferred addition of potassium fluoride.

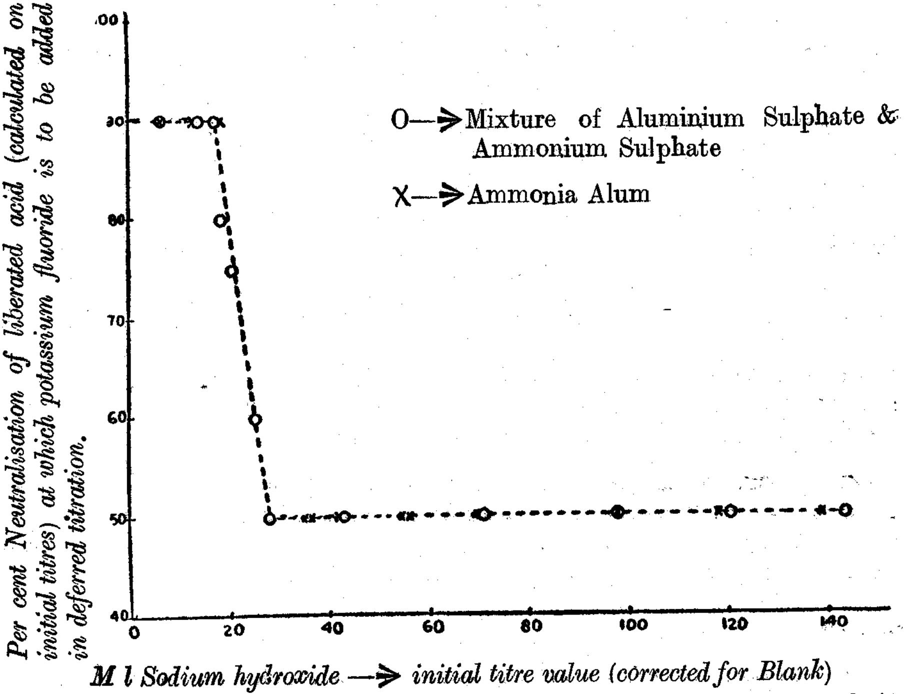

FIG. 1—Graph showing the Point of addition of Potassium Fluoride in Deferred Titration.

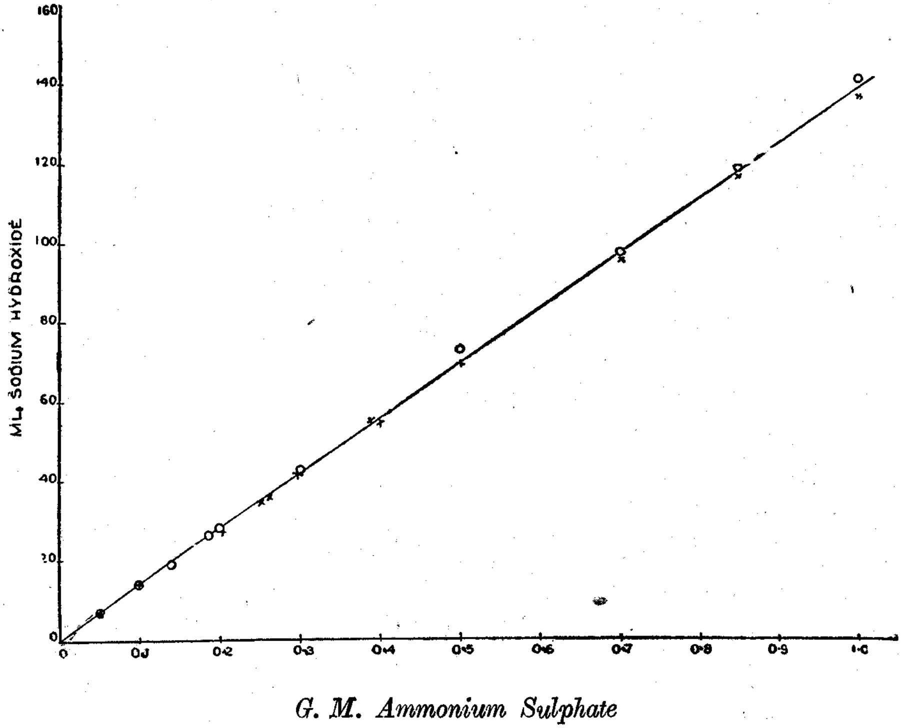

FIG. 2—Graph showing the relationship between concentration of ammonium sulphate and initial titre value.

Results in Tables I & II show that percent sorption is proportional to the concentration of aluminium sulphate. Graph of initial titres vs. concentration of ammonium sulphate is a straight line passing through the origin. This thus establishes a direct relationship between initial titre values and the ammonium sulphate concentration of alum ammonia and gives a direct method for evaluating ammonium sulphate concentration.

With a view to verify the method developed, a series of potentiometric titrations were also carried out using alum/mixture of aluminium sulphate and ammonium sulphate, the concentration of these was adjusted so as to give ammonium sulphate content varying from 0·05 gm to 0·6 gm. The titrations were carried out as per method a (*ii* & *iii*) above.

The results obtained are in conformity with those obtained by titration using indicators. A typical graph using alum, with ammonium sulphate content of 0·3 gm is given in Fig III. The point of neutralisation determined from dpH/dv (Max) falls close to that of change in the indicator colour.

Indicators

It has been found that phenolphthalein indicator changes its colour slowly. One has thus to be very cautious in using this indicator. However, with experience, this indicator gives fairly accurate results.

An alternative mixed indicator consisting of equal volumes of Phenolphthalein, thymolphthalein and BDH 9011, developed by authors has been found to give sharp colour changes at the end point, and is recommended. This indicator changes its colour from pink in acidic alum-formaldehyde solutions through yellow to pink at the end point.

Experiments (Table V refers) have shown that the reaction between ammonium sulphate and formaldehyde is more or less instantaneous. A period of two minutes is, therefore, considered sufficient for the reaction to be completed, after which titration can be carried out. Waiting for half an hour, as recommended for ammonium salt by Rosin[1] is not considered necessary.

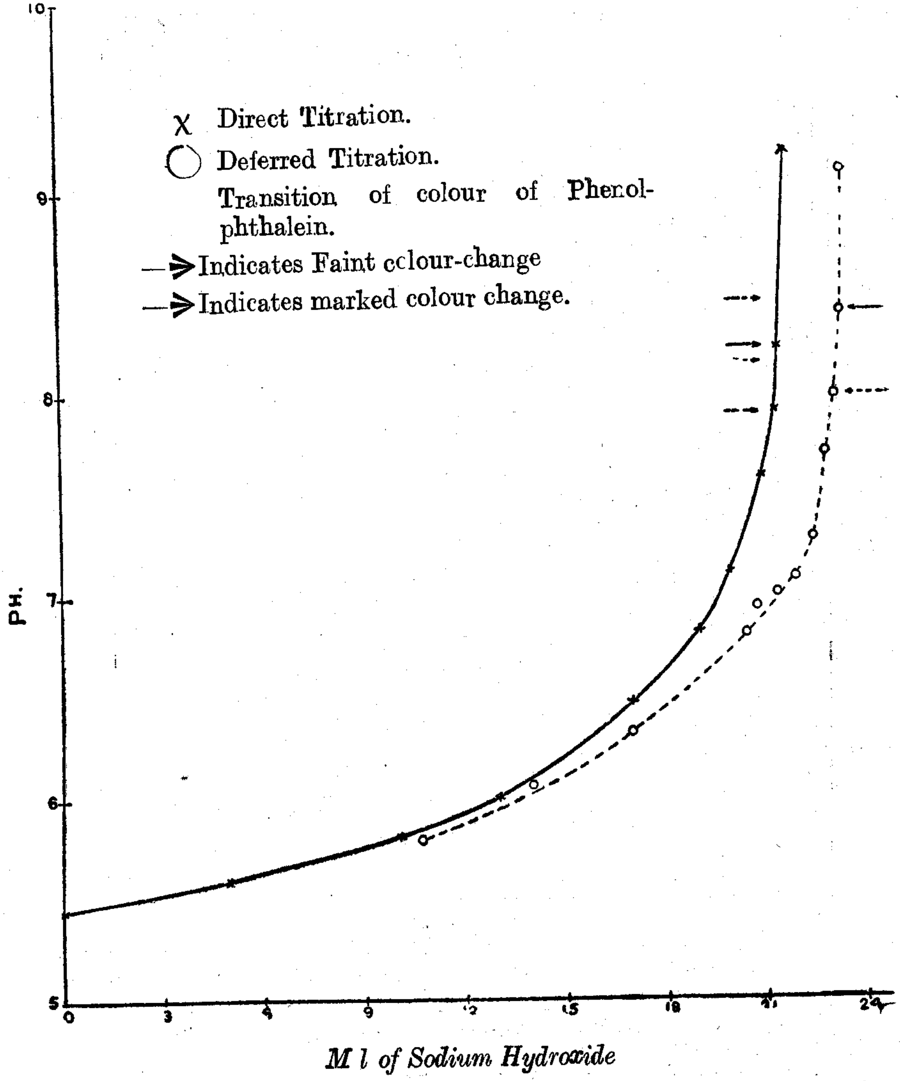

FIG. 3—Graph showing potentiometric determination of ammonium sulphate in ammonia alum.

TABLE I

Results showing the recovery of ammonium sulphate in a mixture of ammonium sulphate and aluminium sulphate by methods under sub-para b, c and d of para 2

Serial No	Amount of aluminium sulphate $Al_2(SO_4)_3$ $18H_2O$ added in g	Amount of ammonium sulphate $(NH_4)_2SO_4$ added in g	Recovery of Ammonium Sulphate by			
			Conventional distillation method	Ammonia expulsion method	Formaldehyde method direct titration	
(I)	(II)	(III)	Per cent (IV)	Per cent (V)	Titre value (initial in Ml NaOH (0·1 N) (VI)	Per cent (VII)
1	0·2500	0·0500	100·80	..	6·9	91·6
2	0·5000	0·1000	99·97	..	13·9	91·6
3	0·6900	0·1380	100·90	..	19·0	91·0
4	0·9400	0·1880	100·40	..	26·1	91·5
5	1·0000	0·2000	101·00	94·0 92·0	28·1	92·9
6	1·5000	0·3000	100·30	97·0 89·5	42·6	93·7
7	2·5000	0·5000	..	99·7 94·8	70·45	93·0
8	3·5000	0·7000	..	..	98·0	93·9
9	4·2500	0·8500	..	..	121·0	94·4
10	5·0000	1·0000	..	..	143·5	94·8
11	2·0000	0·2500	..	73·4 91·5 100·3	..	..

N.B.—1. Serial Nos 7 to 10 and column No VI.

In actual titrations 0·5 N alkali was used to avoid dilution. These titres have been recalculated in terms of 0·1 N alkali and recorded for the sake of comparison.

Serial Nos 7 to 10 column II & III.

10% (W/V) aluminium sulphate solution and 2% (W/V) aluminium sulphate solution were used to avoid dilution.

2. Serial Nos 1 to 6 and column II and III.

5% (W/V) aluminium sulphate solution and 1% (W/V) ammonium sulphate were used.

TABLE II

Results showing the recovery of ammonium sulphate in ammonia alum by methods under sub-para b, c and d of para 2

Serial No.	Amount of ammonia alum $(NH_4)_2$ SO_2 $Al_2(SO_4)_3$ 24 H_2O) added in g	Recovery of Ammonium Sulphate by			
		Conventional distillation method	Ammonia expulsion method	Formaldehyde method direct titration	
		in gms	Per cent	Titre value in Ml of NaOH (0·1 N)	Per cent
I	II	III	IV	V	VI
1	0·3434	0·0500	93·30	6·90	91·0
2	0·6862	0·1000	93·30	13·60	90·0
3	0·7087	0·1033	..	14·05	90·2
4	1·3720	0·2000	96·45	27·80	91·7
5	1·7155	0·2500	100·80	34·80	92·1
6	1·7690	0·2578	95·85	36·00	92·9
7	2·0586	0·3000	..	41·70	92·0
8	2·6850	0·3913	103·60	54·80	92·8
9	2·7448	0·4000	..	55·10	91·0
10	3·4310	0·5000	..	70·00	92·4
11	4·8030	0·7000	..	97·50	92·1
12	5·8320	0·8500	..	118·00	91·7
13	6·862	1·0000	..	139·00	91·7

NOTE: 1. For the purpose of above calculations the percentage of ammonium sulphate as found by the ammonia distillation method column II above has been taken as representing 100% recoveries.

2. Serial Nos 8 to 13 column V : In actual titrations 0·5 N alkali solution was used to avoid dilution. These titres have been recalculated in terms of 0·1 N alkali and recorded for the sake of comparison.

3. Serial Nos 8 to 13, column II : 10% (weight/volume) ammonia alum solution was used to avoid dilution.

4. Serial Nos 1 to 7 column II : 5% (weight/volume) ammonia alum solution was used.

TABLE III

Results of deferred addition of potassium fluoride in a mixture of ammonium sulphate and aluminium sulphate by formaldehyde method

Serial No.	Amount of aluminium sulphate $Al_2(SO_4)_3 \cdot 18H_2O$ added in g	Amount of ammonium sulphate added in g	Percentage of Ammonium sulphate found when fluoride was added at the following stages of neutralisation of the liberated acid calculated on the initial titres								
			A	B	C	D	E	F	G	H	I
			0%	25%	40%	50%	60%	75%	80%	90%	99·5%
1	0·2500	0·0500	91·6	..	..	95·7	..	97·2	..	100·2	104
2	0·3750	0·0750	92·9	..	..	..	..	97·3	..	100·3	102·8
3	0·5000	0·1000	91·6	92·7	93·8	94·6	94·9	97·3	..	100·2	101·7
4	0·6250	0·1250	90·3 91·0	..	..	..	..	97·6	..	100·2	102·0
5	0·6900	0·1380	91·0	..	..	..	..	98·7	100·3	..	102·0
6	0·7500	0·1500	91·1	..	..	..	..	99·1	99·7	101·5	102·5
7	0·8750	0·1750	92·7	..	..	99·1	100·1	..	..	..	106·3
8	0·9400	0·1880	91·5 91·1	..	..	98·9	99·7	100·9	..	..	105·9
9	1·0000	0·2000	92·9	..	..	99·3	..	102·9	..	..	107·6
10	1·2500	0·2500	92·4	..	..	100·1	..	..	..	..	107·2
11	1·5000	0·3000	93·7	..	..	99·9	..	..	..	..	106·6
12	2·0000	0·4000	92·1	95·7	98·7	99·9	102·0	..	..	..	108·3
13	2·5000	0·4998	93·0	..	..	99·4					
14	2·5000	0·5000	93·0	..	..	99·6					
15	3·5000	0·7000	93·9	..	..	100·1					
16	4·2500	0·8500	94·4	..	..	100·2					
17	5·0000	1·0000	94·8	..	..	101·0					

NOTE:—25 ml of K. F. solution (25%) and 5 ml of neutral formaldehyde (40%) were added in each determination.

TABLE IV

Results of deferred addition of potassium fluoride in ammonia alum by formaldehyde method

Serial No.	Ammonium sulphate content of ammonia alum in g	Percentage ammonium sulphate found when potassium fluoride was added at the following stages of neutralisation of liberated acid calculated on the initial titres								
		A	B	C	D	E	F	G	H	I
		0%	25%	40%	50%	60%	75%	80%	90%	99·5%
1	0·0500	91·0	..	..	..	..	..	..	99·1	99·97
2	0·1000	90·0	..	..	..	..	..	..	99·97	103·3
3	0·1033	90·2	92·7	..	96·0	..	98·5	..	100·3	103·3
4	0·2000	91·7	..	..	100·2	..	..	..	..	107·7
5	0·2500	92·1	..	..	100·3	..	..	..	..	108·0
6	0·2578	92·9	96·5	98·2	99·7	..	102·9	..	..	107·6
7	0·3000	92·0	..	..	100·3	..	..	..	..	108·6
8	0·3913	92·8	..	100·3	100·9	..	..	..	..	108·1
9	0·4000	91·0	..	..	100·2	..	..	..	..	109·1
10	0·5000	92·4	..	..	100·0	..	..	..	..	..
11	0·7000	92·1	..	..	99·7	..	..	..	..	..
12	0·8500	91·7	..	..	100·6	..	..	..	..	..
13	1·0000	91·7	..	..	99·6	..	..	..	..	..

N.B.—25 ml of KF solution (25%) and 5 ml of neutral formaldehyde (40%) were added in each determination.

TABLE V

Results showing rate of reaction of formaldehyde and ammonium sulphate (in the mixture)

Serial No.	1	2	3	4	5
Duration of reaction in minutes	1	2	3	4	30
Percent recovery of ammonium sulphate by formaldehyde direct titration method.	90·8	92·5	92·5	92·5	92·5

N. B.—5 ml of ammonium sulphate solution (1·0°/o W/V), 5 ml of aluminium sulphate solution (0·5°/o W/V), 5 ml of formaldehyde solution (40°/o W/V neutral), 10 ml of potassium fluoride solution (25°/o W/V), and 3 ml of mixed indicator were used for each determination.

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References

1. Rosin Joseph, *Reagent Chemicals and Standards* (pp. 31, 37, 50 & 51) 3rd Ed., 1955. (D. Van. Nostrand Co., New York).
2. *ANALAR Standards for Laboratory Chemicals*, 5th Ed. 1957 (P. 44), British Drug Houses Ltd. & Hopkin & William Ltd., London.
3. Aldo Rusconi (Lab. Beghee Chiapetta, Milan, Italy), *Climica* (Milan), **5**, 107, 1950.
4. Koszegi, D. and Salgo, E., *Acta. Chim., Acad. Sci. Hung.*, 7, 333, 1955.
5. Graham, R.P., *J. Industrial & Engg. Chemistry,* Analytical Ed., P. 472, Aug. 1946.
6. Caron, H. and Raquet, D., *Chim. Anal.*, **30**, 61, 1948.
7. Kazumi Kondo, *Japan Analyst*, **3**, 38, 1954.
8. Amir Chand et al, *D. Sc. Jour.*, 12 (No. 1), 1961.