

Bulletin No. 26.

WITH THE COMPLIMENTS OF THE DIRECTOR  
INDIAN LAC RESEARCH INSTITUTE  
BANKEN, RAIPUR, S.O.  
INDIA

THE

# Indian Lac Research Institute



## ESTIMATION OF ORPIMENT IN SHELLAC

BY

M. RANGASWAMI and H. K. SEN.



Calcutta:  
1937

Price 2 Annas.

# ESTIMATION OF ORPIMENT IN SHELLAC

BY

M. RANGASWAMI AND H. K. SEN.

**Introduction.**—In the manufacture of most commercial grades of shellac, it has been the practice to mix the seed lac with a small proportion of orpiment or arsenious trisulphide. Although shellacs generally contain 0.1–0.3% of arsenious sulphide, one occasionally comes across samples containing as much as 0.8–1%.

As is well-known, the practice of mixing shellac with orpiment is resorted to in order to give a lighter colour to the shellac. The presence of orpiment, however, does not only not confer any permanent benefit on the shellac but, on the contrary, exercises a deleterious effect on the properties of the film, unless removed by filtration<sup>1</sup>. Besides, the orpimented shellac has been found to take more bleach to get a desired effect owing to the presence of the orpiment<sup>2</sup>. The possible poisonous effects of the orpiment in shellac in an industry like canning has also long been noticed. These facts have for some time been recognised in the trade and an effort is being made to restrict wholly or within limits the admixture of shellac with orpiment. The estimation of orpiment is, therefore, of great importance in the routine analysis of shellac and in the present paper has been described a reliable method for the estimation of arsenic in small quantities of shellac, which eliminates many of the inconveniences of the existing methods without loss of accuracy.

So far, the most important method of determining orpiment in shellac, when present in appreciable quantities, is the official method of the United States Shellac Importers' Association<sup>3</sup>. This method is found to be long and tedious and, owing to the need for the constant attention of the analyst during the distillation, is not suitable for running more than one estimation at a time. Besides, the inconvenience of working with acid fumes is a factor which requires elimination.

A more rapid and convenient method is an iodimetric method employed by the Association of the official Agricultural Chemists, slightly modified in detail at Namkum for the estimation of orpiment in shellac<sup>4</sup>. Although 4 estimations can be run simultaneously by this method and completed in 6–8 hours, 1.3 gms. of shellac are required for an estimation and the inconvenience caused by the fumes of  $\text{NO}_2$  and  $\text{SO}_3$  during the digestion with acids has not been eliminated.

A more suitable semi-micro method has now been developed, on the basis of the iodimetric titration of arsenic, in which the estimation of  $\text{As}_2\text{S}_3$  is carried out on smaller quantities of shellac in a special fumeless apparatus devised for the purpose.

**Description of the Apparatus.**—The apparatus (See Sketch) consists of a stout, vertical, Pyrex glass tube, A, closed at one end and drawn out at the other to a narrow tube, B. A little above the narrow end, a side tube, C, is provided for connecting it with an ordinary glass filter-pump. A small hole may be made in C for pressure

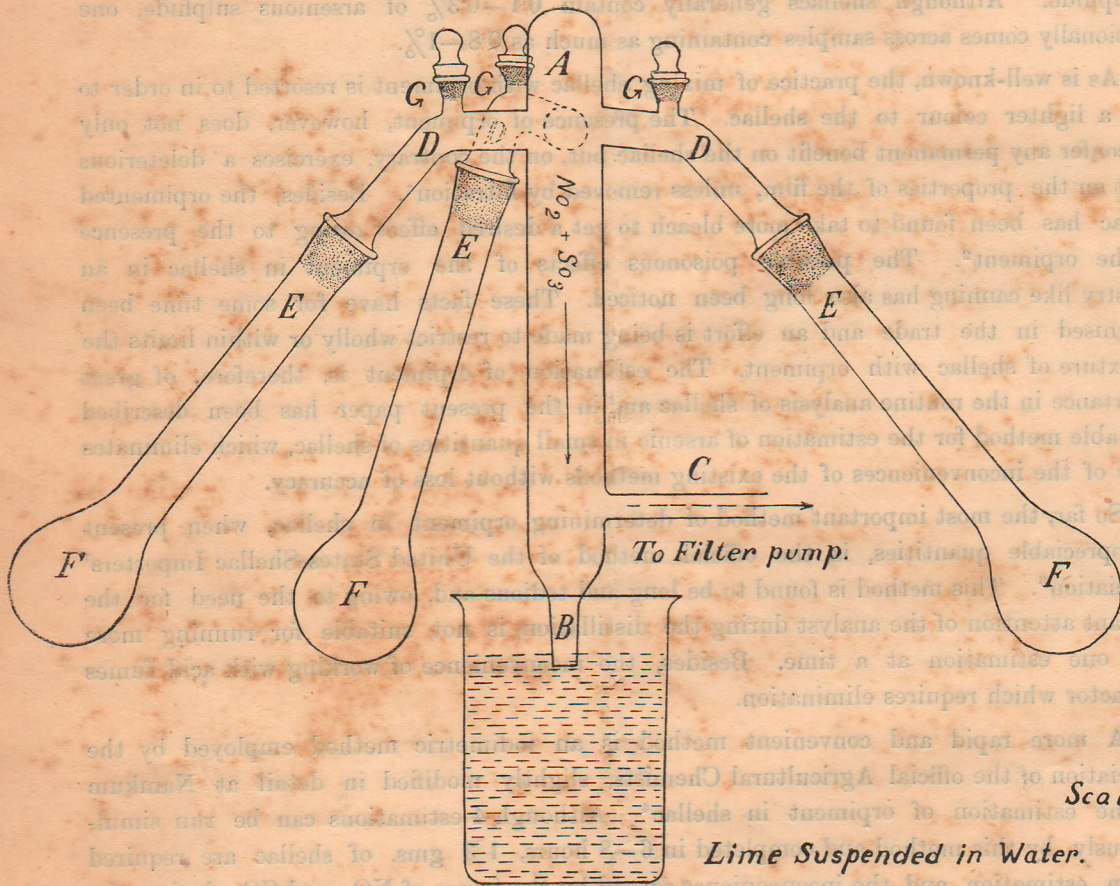
# ESTIMATION OF ORPIMENT IN SHELLAC

BY

M. RANGASWAMI AND H. K. SEN.

**Introduction.**—In the manufacture of most commercial grades of shellac, it has been the practice to mix the seed lac with a small proportion of orpiment or arsenious sulphide. Although shellac generally contains 0.1–0.3% of arsenious sulphide, one occasionally comes across samples containing as much as 1.5%.

As is well-known, the practice of mixing orpiment with shellac does not only give a lighter color to the shellac, but also increases its viscosity. It is therefore not correct to say that orpiment is added to shellac for the purpose of increasing its viscosity. The practice of mixing orpiment with shellac has been found to be a serious defect in the manufacture of shellac, as it has a deleterious effect on the properties of the film. It has been found that shellac containing orpiment is more liable to be attacked by insects than shellac free from orpiment. The orpiment is also a poison to many of the insects which are used in the industry like cutting wasps. The orpiment is also a poison to many of the insects which are used in the industry like cutting wasps. The orpiment is also a poison to many of the insects which are used in the industry like cutting wasps.



So the most important factor in the estimation of orpiment in shellac is the presence of arsenious sulphide. The orpiment is also a poison to many of the insects which are used in the industry like cutting wasps. The orpiment is also a poison to many of the insects which are used in the industry like cutting wasps. The orpiment is also a poison to many of the insects which are used in the industry like cutting wasps.

A more rapid and convenient method for the estimation of orpiment in shellac has been developed. The method is based on the principle that orpiment is soluble in a solution of lime suspended in water. The orpiment is dissolved in the solution, and the amount of orpiment is determined by titrating the solution with a standard solution of potassium dichromate.

A more suitable semi-micro method has now been developed, on the basis of the iodometric titration of arsenic in which the estimation of  $As_2S_3$  is carried out on smaller quantities of shellac in a special funnelless apparatus devised for the purpose.

**Description of the Apparatus.**—The apparatus (See Sketch) consists of a stout vertical Pyrex glass tube A, closed at one end and drawn out at the other to a narrow tube B. A little above the narrow end a side tube C is provided for connecting it with an ordinary glass filter-pump. A small hole may be made in C for pressure

Scale 4"-1"

Lime Suspended in Water.

equalisation in the system during digestion. A few inches below the top-end are fused three tubes, D, bent to an angle of  $120^\circ$ , the other ends of which are widened and provided with ground joints, E, to fit into the necks of the three 100 c.c. Pyrex Kjeldahl flasks, F. The bent tubes are each provided with a ground stopper, G, by the removal of which, successive instalments of nitric acid could be added without disconnecting the flasks from the apparatus. The narrow end, B, is just dipped into water containing lime or any other alkali in a beaker in order to absorb any acid fumes not removed by suction.

**Sampling.**—After an average sample has been collected from a case or a consignment according to the U.S.S.I.A. method of sampling<sup>3</sup>, it should be successively crushed finer and finer, and every time the whole of the crushed lot should be carefully mixed, till about 50 grams of sample are finally collected. This is powdered to pass through a 100 mesh sieve. The powdered sample is then entirely transferred to a piece of glazed paper and well mixed by rolling it several times. The heap is thinly spread on the paper and a smaller representative sample is made up on another piece of paper by collecting small lots of the powder from various portions of the heap. The sample so obtained is again thoroughly mixed by rolling and a still smaller sample is prepared as before. Sampling is carried out in this way until a representative sample of about 5 gms. of shellac is ultimately obtained. This is well mixed again before transferring to a small weighing bottle, from which suitable quantities are removed by means of a small glass spoon resting in the weighing bottle.

**Experimental details.**—The actual determination is carried out as follows:—

0.5—1 gm. of the shellac, according to the orpiment content of the sample, is carefully tipped into each of the digesting flasks, F, of the apparatus. 2-3 c.c. of pure As-free  $H_2SO_4$  are then added to each flask and mixed with the shellac for a short while. A few c.c. of pure concentrated  $HNO_3$  are then added, taking care that any material sticking near the neck is washed down into the flask. The flask is continuously agitated until the vigorous evolution of the nitric acid fumes ceases and the shellac goes into solution in the acid mixture. With only 0.5 gm. of shellac or less, the flasks could be placed in position immediately after the addition of  $HNO_3$  but with larger quantities of shellac it is advisable to carry out this part of the procedure outside, preferably under a flue, in order to avoid the risk of the shellac frothing considerably. The flasks are then connected to the apparatus and supported on retort ring and wire-gauze in such a way that there is no strain in the apparatus.

Heating is now commenced, applying gentle suction by the water pump at the same time. Very rapid heating should at first be avoided but when the solutions begin to boil steadily, heating could be increased sufficiently to keep them boiling vigorously. When the evolution of brown fumes is followed by the white fumes of  $SO_3$  and the solution shows signs of spurting, heating is momentarily suspended and the ground stopper G removed. 10 c.c. of  $HNO_3$  is slowly run in through the opening by means of a small funnel with a bent stem and heating is resumed after replacing the stopper in position. Additions of  $HNO_3$ , followed by strong heating, is continued until the solution in the flasks turns colourless and copious white fumes of  $SO_3$  are given off. The oxidation of the last traces of organic matter is assisted by the addition, towards the end, of a pinch of  $NaNO_3$  and continuing the heating until the evolution of brown fumes ceases. The digestion usually takes  $1\frac{1}{2}$ —

2 hours, but by using fuming nitric acid, a reduction of 20 minutes in the period of digestion has been observed.

The flasks are then allowed to cool for a few minutes and the  $\text{HNO}_3$  remaining in solution is expelled by boiling twice or thrice with small quantities of water (introduced *via* G) until white fumes of  $\text{SO}_3$  are given off each time. It is essential to add a few pieces of clean pumice stone to the solution in order to avoid the violent bumping which would otherwise result at this stage. It should be remarked also that boiling with water should not be done until the digestion in the other flasks is also complete as otherwise the steam issuing during boiling will dilute the acid in the other flasks and prolong the digestion.

The flasks are now removed from the apparatus and the solution is diluted with about 50 c.c. of pure distilled water. The arsenic which is now present as  $\text{As}_2\text{O}_5$  is reduced to  $\text{As}_2\text{O}_3$  by means of a small crystal of KI and the liberated iodine is nearly all expelled by boiling the solution until it attains a pale-yellow colour. The solution is again diluted to about half the volume of the flask and the residual colour of iodine is just discharged by the careful addition of N/100  $\text{Na}_2\text{S}_2\text{O}_3$ , using a few drops of starch solution as indicator.

The solution is immediately neutralised by the gradual addition of solid  $\text{NaHCO}_3$ . An excess of 2-3 gms. of  $\text{NaHCO}_3$  is added and after the addition of 2-3 c.c. of freshly prepared 1% starch solution, the solution is titrated against N/100 Iodine.

The iodine solution used for titration is previously titrated against a standard sulphuric acid solution of  $\text{As}_2\text{O}_3$  of similar strength and standardised in terms of  $\text{As}_2\text{S}_3$  per c.c. of iodine solution

**Results of tests.**—To test the accuracy of the method, several determinations were carried out on commercial samples of shellac as well as on samples specially prepared by mixing known quantities of pure shellac and pure precipitated  $\text{As}_2\text{S}_3$ . The following table indicates the excellent agreement of the results among themselves and between the amounts of orpiment present in the samples and the amounts estimated by this method.

Table I.

## Determinations of Orpiment in Shellac by the New Method.

Expt.	Sample.	Weight taken for Estimation.	As <sub>2</sub> S <sub>3</sub> Estimated.	As <sub>2</sub> S <sub>3</sub> Present.
1.	Shellac L 256	1.3546 gm.	0.91%	0.93%
		1.0032	0.93	
		0.6321	0.91	
		0.5749 gm.	0.31%	0.33%
		0.4961	0.32	
2.	Shellac L 257	0.5749 gm.	0.31%	0.33%
		0.4961	0.32	
		0.5033	0.35	
		0.6750	0.30	
		0.5426	0.30	
		0.5330	0.32	
3.	Sample prepared by mixing shellac with 0.20% pure As <sub>2</sub> S <sub>3</sub>	0.6517 gm.	0.20%	0.20%
		0.4974	0.22	
		0.5324	0.22	
		0.5526	0.20	
		0.5065	0.19	
		0.4894	0.20	
4.	Shellac and pure As <sub>2</sub> S <sub>3</sub> separately weighed out into the flask	0.6570 gm.	5.86 mgms.	5.7 mgms.
		0.4867	5.19	5.0
		0.6177	4.10	4.3
		0.3804	3.26	3.4
		0.4262	2.90	3.0
		0.5078	5.28	5.1

N. B.—The figures for % As<sub>2</sub>S<sub>3</sub> present in Expts. 1 and 2 are based on determinations made by the Namkum method.<sup>4</sup>

**General discussion.**—It should be mentioned that very thorough sampling and great care in manipulation are essential for getting accurate and concordant results. However, once the representative samples are weighed out into the flasks, the procedure is quite simple and three estimations could be conveniently completed in about 3½ hours. This compares favourably with the Namkum method<sup>4</sup> which would take 6—8 hours for four estimations and the American method<sup>3</sup> would take perhaps much more than a working day for each determination.

As regards samples containing less than 0.2% orpiment, 0.5 gm. of a 0.2% sample will contain 1 mgm. of  $As_2S_3$  which is equivalent to only 1.65 c.c. of N/100 Iodine. The degree of accuracy might, therefore, be appreciably reduced in the case of shellacs containing much less than 0.2%  $As_2S_3$  and it would be preferable in these cases to increase the weight of shellac to 1 gm. for each estimation. The possibility also exists of reducing the strength of the iodine solution further to N/200 since a few good results have been obtained on these lines.

Samples containing less than 0.1% are best tested by the following modification of the method described above :—

5 gms. of the representative sample are weighed out into a beaker and dissolved in 100-125 c.c. of 95% alcohol on a water-bath. The hot solution is filtered through a fairly close-textured filter paper well-fitted into a glass hot-water funnel. The stem of the funnel is fitted into a Buchner flask and gentle suction is applied during the filtration. Allowing a little time for the wax to settle and first decanting the clear solution into the filter considerably facilitates the filtration. The impurities including orpiment, sand, etc. are transferred to the filter by washing down with successive quantities of hot alcohol. The filter paper containing the orpiment is removed, folded, dried and introduced into the digesting flask of the apparatus for further treatment as described before. The filtration and washing will not normally take more than about 20 min. and actual tests have shown that filtration of the alcoholic solution does not result in an error of any appreciable degree.

The possibility of interference in the accuracy of orpiment estimation due to the presence of iron in some samples of shellac was examined and experiments with known amounts of ferric sulphate added to standard solutions of sodium arsenite as well as to orpimented shellac gave no variation in the arsenic content as would be seen from the following table :—

Table II.

## Influence of Iron on Orpiment Estimation.

	Shellac.	Sodium arsenite added (approximate strength).	*Ferric Sulphate solution added.	As <sub>2</sub> O <sub>3</sub> found.	
1.	Nil	1 c.c.	N/10	Nil	5.08 mgms.
2.	"	"	"	1 c.c.	5.08 "
3.	"	"	"	"	4.93 "
4.	"	"	"	"	5.25 "
5.	"	"	"	"	5.15 "
6.	"	10 c.c.	N/100	Nil	5.10 "
7.	"	"	"	1 c.c.	5.05 "
8.	"	"	"	2 c.c.	5.05 "
9.	0.5760 grams	1 c.c.	N/10	Nil	5.08 "
10.	0.5777 "	"	"	"	5.08 "
11.	0.5735 "	"	"	1 c.c.	5.10 "
12.	0.6862 "	10 c.c.	N/100	Nil	5.08 "
13.	0.6374 "	"	"	1 c.c.	4.98 "
14.	0.6553 "	"	"	2 c.c.	5.08 "
15.	0.4930 (Orpimented)	"	Nil	Nil	0.955% (As <sub>2</sub> S <sub>3</sub> )
16.	0.5240 "	"	"	1 c.c.	0.963% "
17.	0.5106 "	"	"	2 c.c.	0.946% "
18.	0.7088 "	"	"	Nil	0.486 "
19.	0.6452 "	"	"	Nil	0.477 "
20.	0.5868 "	"	"	2 c.c.	0.489 "
21.	0.6412 "	"	"	Nil	0.485 "
22.	0.6167 "	"	"	"	0.485 "

\* NOTE.—1 c.c. of ferric sulphate solution, added for introducing iron as impurity, contained 0.00033 gram of Fe<sub>2</sub>O<sub>3</sub> which corresponds to approximately 0.066% in shellac. This is very much more than the percentage of ferric oxide usually found in commercial samples of shellac.

Experiments 15, 16 and 17 were performed on the same commercial sample of shellac; similarly, 18, 19, 20, 21 and 22 were on the same commercial sample but different from the previous one.



In conclusion, it should be pointed out that the apparatus described above is also of a more general application than for the estimation of orpiment in shellac. As it is primarily devised for the fumeless destruction of organic matter, it should be eminently suitable for all work of that kind and particularly for the acid digestion of small quantities of organic substances for the Kjeldahl estimation of nitrogen.

#### Summary.—

1. The importance of finding an easy, convenient, rapid and accurate method for the estimation of orpiment in shellac is briefly indicated.
2. The present well-known and recognised methods of determining orpiment in shellac have been found to be not quite suitable for *routine analysis* from the point of view of simplicity, rapidity, economy of material and exposure to acid fumes.
3. A modified iodimetric method of carrying out an estimation on only 0.5—1 gm. of shellac has been described, which combines rapidity and ease of manipulation without impairing the accuracy of the estimation.
4. An apparatus has been devised in which three estimations could be carried out in the open laboratory without the undesirable exposure to acid fumes.
5. A modification of the new method has been suggested in the case of shellacs containing very small quantities of orpiment, by which larger quantities of the sample could be dealt with in the same apparatus.
6. The suitability of the same apparatus for the fumeless digestion of small quantities of organic substances for the Kjeldahl estimation of nitrogen is also indicated.

#### References.—

1. M. Rangaswami : The Influence of Orpiment in Shellac on the Protective Properties of the Varnish, Bull. No. 10, Ind. Lac. Res. Inst., P. 7, (1932).
2. R. W. ALDIS : Orpiment in Shellac, Bull. No. 13, Ind. Lac Res. Inst., P. 2, (1933).
3. THE UNITED STATES SHELLAC IMPORTERS ASSOCIATION AND THE AMERICAN BLEACHED SHELLAC MANUFACTURERS' ASSOCIATION : Official methods of Analysis, Specifications and General Information on Shellac and Bleached Shellac, (1934).
4. M. RANGASWAMI AND R. W. ALDIS : Orpiment and the Iodine Value of Shellac, Bull. No. 7, Ind. Lac Res. Inst., P. 2, (1932)

February 1937.

INDIAN LAC RESEARCH INSTITUTE, NAMKUM,  
RANCHI, INDIA.