

A Method for the Dry Assay of Sulphides and Oxides of Lead and Bismuth

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SYNOPSIS—A rapid test tube method of dry assay of lead in galena is based on the observation that if a solution of galena in molten caustic potash is heated with stannous sulphide the lead is quantitatively reduced to metal and may be obtained as a button. The method is applicable also to the oxides of lead. Bismuth in its oxide or sulphide may be similarly assayed. The action of the stannous chloride is discussed: heated alone with molten caustic potash it is entirely oxidised to the stannic state with evolution of hydrogen.

PELLETS of caustic potash melt at 170° C. If galena is present, it begins to dissolve at once in the molten alkali and there is formed, with mineral of high grade, a clear solution, coloured more or less red according to whether the galena contains much or little iron. The solution contains lead oxide and potassium sulphide and addition of water to it reverses the reaction, the black sulphide being precipitated.

When caustic potash and stannous sulphide are slowly heated together the alkali, as soon as it is melted, attacks the stannous sulphide and hydrogen is liberated, increasing in quantity as the temperature rises and producing at 180° to 190° C. vigorous effervescence. The melt is clear and yields a clear solution with water. On acidification, hydrated stannic oxide, with perhaps some stannic sulphide, is precipitated. No stannous compound is formed in this reaction.

In presence of galena the reaction between the alkali and stannous sulphide is modified, in so far as the yield of hydrogen is greatly reduced; at the same time metallic lead is separated quantitatively. This reaction is suggested here as the basis of a method for the assay of galena and it has also been found capable of extension to the oxides of lead and to the sulphide and oxide of bismuth.

METHOD—

The operation is carried out in a test tube and the composition of the charge found most suitable, having regard to accuracy of result, ease of manipulation and economy of time is: PbS 0.35 g., SnS 0.70 g. and KOH 4.0 g. The galena, crushed to pass a 60- or 80-mesh sieve, is shot into the test tube down a chute of glazed paper and the potash pellets are added and melted in a small flame, a roll of filter paper being placed in the tube to absorb moisture. When the galena has dissolved, or nearly so, the paper is removed and the charge of stannous sulphide added in 5 or 6 portions through a small funnel; the heating and swirling of the tube are so regulated that the froth, caused by the escape of hydrogen, does not rise more than about an inch up the tube, and particles of stannous sulphide, borne upwards on the froth, subside into the liquid. The lead soon separates as a spongy mass and the heating is increased gently until the melting-point of lead (327° C.) is reached. The metal then appears as a brilliant bead in a translucent liquid and the reaction is complete. After solidification the melt is dissolved in water, the muddy liquid decanted and the bead cleaned with a little dilute hydrochloric acid, dried on filter paper and weighed. The whole operation can be done in 5 to 10 minutes. If the tube should spring a small leak after the lead has separated, but before complete melting, the sponge can be extracted, pressed between filter papers and heated with a small amount of potash, and the metal recovered without loss. It may be mentioned that it seems necessary, in order to get accurate results, that the galena should be dissolved, or nearly so, in the potash before the addition of the reducing agent. Early experiments in which the two were ground finely together gave results almost invariably 1 or 2 per cent. low.

The method has been tested on three samples of galena: (a) a selected cleavage cube without visible impurity, (b) a high-grade concentrate from Sipton, Northumberland, and (c) a low-grade concentrate from Halkyn, Flintshire, containing much dirty gangue and blende. The dry assay by the ordinary crucible method was done on (b) and (c), and the determination of lead by wet methods on all three. The results, as percentages of lead, are given below. Those by the new method are from three consecutive trials and the means of these.

Sample	Crucible assay %	Wet assay %	New method, %				Mean
(a)	—	85.0	85.1,	85.3,	84.6		85.0
(b)	79.8	82.8	83.0,	83.3,	82.3		82.9
(c)	57.5	61.3	61.2,	61.2,	60.9		61.1

Some experiments have been made on the effect of adding to the charge sulphides, commonly associated with galena, that are easily reducible and yield metals soluble in lead at a relatively low temperature. These were added in such quantity as would give, on complete reduction and absorption by the lead, an alloy containing 3 per cent. of the metal. The effect of addition of orpiment was not reflected in the quantitative results and the bead was malleable and contained little more than a trace of arsenic. With stibnite somewhat more antimony was found in the bead, but its weight was not seriously affected. It is probable that these sulphides form sulpho-salts not easily reduced. With bismuth sulphide, however, there was complete reduction to bismuth, which was taken up by the lead.

Application to oxides of lead—Peroxide of lead is "balled up" by the potash and appears to be but slightly soluble in it, but this does not affect its reducibility. The two other oxides are fairly soluble. The method used is the same as for galena, but it is advantageous to

increase the quantity of stannous sulphide to 1 g. and that of potash to 5 g. The experimental results, given below as percentage of lead, show good agreement with those from the wet assay.

				Wet assay %	New method %
PbO	89.8	90.0, 90.1
Pb ₃ O ₄	89.4	89.6, 89.8
PbO ₂	85.6	85.3, 85.0

Application to sulphide and oxide of bismuth—The reaction with these compounds goes rather more easily than with the compounds of lead, being facilitated by the low melting-point of the metal (268° C.). The charge is as for galena. Some results, as percentages of bismuth, are given below.

				Wet assay %	New method %
Bi ₂ S ₃	77.5	77.7, 77.6, 77.4
Bi ₂ O ₃	89.5	89.0, 89.2, 89.2

The experimental results cited above attest the value of this reaction as a quantitative one. The obvious advantages lie in the economy of material and fuel and the great saving in time. Duplicate determinations of galena, for example, can be completed in 30 to 40 minutes, including the weighings, and the requisite skill for rapid and successful operation is easily acquired. Perhaps the only drawback with galena is that the silver cannot be determined in the bead. Metallic tin brings about the same reaction as stannous sulphide, but it cannot be used in its place, first because of slow reaction, and secondly because some tin is dissolved by the precipitated lead and protected thereby from reaction with the potash. A bead obtained in this way was found to contain 20 per cent. of tin.

NOTE ON STANNOUS SULPHIDE—

The material bought as stannous sulphide and used in these experiments is uniform, black, lustrous and well crystallised; it contains but little impurity. It is, however, not pure stannous sulphide, but a mixture, obviously a solid solution, of stannous and stannic sulphides. The analytical figures are: Sn (total) 74.4, S 24.5 (98.9), Sn (stannous) 57.3 per cent. From these the proximate composition is calculated as: SnS 73.5 and SnS₂ 26.5 per cent., or perhaps more accurately as: SnS 51.6 and Sn₂S₃ 48.4 per cent. For the sake of simplicity the trade name stannous sulphide* has been used in the foregoing account, but it is desirable in what follows to distinguish it from pure stannous sulphide and it may be conveniently, if loosely, termed "tin sulphide." Experiments on the liberation of hydrogen from tin sulphide and potash are informative and throw some light on the reactions involved in the method of assay. The volume of hydrogen equivalent to 1 g. of tin is calculated as 188 ml. at N.T.P. One gram of tin sulphide contains 0.573 g. of stannous tin and should therefore yield 107.7 ml. of hydrogen. The volume actually observed was 107.5 ml., in excellent agreement with this. In presence of added PbS (the two ground together finely) the volume of hydrogen was greatly reduced, being 64.7 ml. from a 2 : 1 mixture and 19 ml. from a 1 : 1 mixture. If the mixing were of the intimacy inherent in a solid solution, then further diminution in the yield of hydrogen would be expected. A suitable solid solution for testing this was made by heating together lead and tin sulphide. The preparation contained a small amount of Pb - Sn alloy and its proximate composition was: PbS 48.9, SnS 45.6, Pb 4.3 and Sn 1.2 per cent.; total Pb 46.7 per cent., total Sn 37.1 per cent. This material with molten potash gave 23.5 ml. of hydrogen per g. and 45.1 per cent. of Pb. Calculating from the hydrogen value, the amount of SnS destroyed by the alkali and hence the residue available for reduction can be found. This is equivalent to 47.1 per cent. of PbS, and would thus yield 40.8 per cent. of Pb. Adding the free lead to this gives the total reduced lead as 45.1 per cent., which is identical with the observed value.

When the same solid solution was ground with its own weight of PbS and melted with alkali, not a trace of hydrogen was evolved and the yield of lead was 69.0 per cent. The whole of the tin was there employed in the reduction, the lead equivalent of which is 64.8. Adding to this the free lead gives the total yield as 69.1 per cent., a figure almost identical

* This reagent was supplied by The British Drug Houses Limited, who will guarantee supplies to contain not less stannous sulphide than that used in these experiments.

with the observed value. These results have been substantiated by similar tests with another solid solution, richer in tin and poorer in lead, the details of which may be omitted.

It is evident that the reducing action of stannous sulphide in these reactions is not brought about by hydrogen, but that the active agent is stannous oxide. This, in molten alkali, is oxidised by water; but when oxides of lead and bismuth are present, these act directly as oxidising agents. There is a further possibility that in some cases the stannous oxide suffers self-oxidation and reduction, yielding stannic oxide and tin and that the latter plays the part of the reducing agent. With tin sulphide, the presumed constituent of the sesqui-sulphide is resolved into stannous and stannic sulphides and the latter, being converted directly into stannic oxide, has no influence on the reduction process.

NOTE ON BEHAVIOUR OF MOLYBDENUM SULPHIDE—

Since the work described above was carried out, I have examined the reaction between MoS_2 and caustic potash. The molybdenum sulphide was prepared from molybdenite and contained 56.4 per cent. of molybdenum, equivalent to 94 per cent. of MoS_2 . This yielded when melted with potash 127 ml. of hydrogen per gram, that is 135 ml. for the pure sulphide. This is close to the calculated yield of 139 ml., based on the assumption that MoS_2 is converted into MoO , which is then oxidised by water, as is SnO .

When MoS_2 is fed into the melt of PbS and KOH , lead separates as a sponge in a sludge greatly thickened with molybdenum compounds. It seems impossible to melt this lead owing to the excessive frothing that takes place towards the end of the reaction. The sponge can, however, be recovered and melted into a bead with a little fresh caustic potash, but the yield is low, of the order 80 per cent. The reaction is therefore useless for quantitative work.

It may be mentioned that FeS_2 does not yield hydrogen with caustic potash, nor is it capable of reducing PbS in the alkali melt.

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February, 1949