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Determination of Barium in AAA [Pitchblende] Gangue

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Determination of Barium in AAA Gangue

In development work with AAA ore, a sulfuric acid precipitation of calcium, barium, strontium, lead and My is performed. The resulting "sulfate cake" must conform to a certain limit with respect to barium, therefore there is a necessity for an accurate barium determination. Since there are no really good methods for separating calcium, strontium and barium from each other (1), it was thought best to investigate the problem.

In order to obtain a relatively pure solution of barium salt, silica must be removed with HF. The lead sulfate must also be removed from the sulfates of calcium, strontium and barium. This may be done with ammonium acetate (2). The remaining sulfates are fused with Na_2CO_3 and the Na_2SO_4 leached with H_2O. $BaCO_3$, $CaCO_3$ and $SrCO_3$ are dissolved in dilute HCl and the barium precipitated with $K_2Cr_2O_7$. Calcium is quite easily separated at this point, as a $CaCrO_4$ precipitation is favored by a basic medium, but strontium is precipitated with the barium. A double precipitation of $BaCrO_4$ is recommended to separate strontium chromate from the $BaCrO_4$ (3,4). At this point, barium may be determined by 1-titrating the excess $K_2Cr_2O_7$, 2-dissolving $BaCrO_4$ in .1N $FeSO_4.(NH_4)_2SO_4$, and titration of the excess ferrous salt with $Ce(SO_4)_2$, 3-dissolving $BaCrO_4$ in HCl and titrating $Cr_2O_7^{=}$ with $FeSO_4$ (5).

Experimental Works

At the outset of the problem, there appeared to be only three portions of the procedure to be investigated, namely, the choice of a method for determining barium at the chromate steps, the separation of strontium chromate from the barium chromate, and a clean separation of lead sulfate from the other sulfates. These conditions were investigated and are described in detail below.

Volumetric Determination of Barium

To 10 ml of BaO standard (99.8 mgm), was added 25 ml 3N HCl and 1 drop of bromphenol blue. The solution was made slightly basic, then faintly acid with acetic acid. 10 ml 3N ammonium acetate were added(6), and the solution brought to boiling. (In all work which follows, the solution to be analyzed for barium was prepared in this manner and the final volume before precipitation with $K_2Cr_2O_7$ was less than 50 ml.) The barium was then precipitated with 50 ml .1N $K_2Cr_2O_7$, the $BaCrO_4$ filtered off, and the filtrate acidified with H_2SO_4. The excess $K_2Cr_2O_7$ was then titrated with $FeSO_4$. All determinations done in this manner showed the presence of $BaSO_4$ in the titrated solution. Time did not permit to effect a satisfactory reason for the presence of $BaSO_4$ at this point. Rather it was decided to proceed to a gravimetric analysis of barium.

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Gravimetric Determination of Barium.

As a result of the work on the volumetric determination, it was thought best to investigate a gravimetric method. Solutions containing 99.8 mgm BaO were prepared as discussed under the work on volumetric determinations. 20 ml 10% $K_2Cr_2O_7$ were added, the $BaCrO_4$ collected on a fine sintered glass crucible and dried at 110°C. See Table I.

Table I

Precipitation of Barium with $K_2Cr_2O_7$.

mgm BaO introduced	mgm BaO Recovered
99.8	104.4
99.8	104.4
99.8	103.8

Ave. = 104.2 ± .3

Since these results seemed high, the barium was precipitated with $(NH_4)_2Cr_2O_7$ according to Hillebrand and Lundell (8). See Table II.

Table II

Precipitation of Barium with $(NH_4)_2Cr_2O_7$

mgm BaO Introduced	mgm BaO Recovered
99.8	104.5
99.8	105.2
99.8	105.2
99.8	104.5

Ave. = 104.9 ± .3

Ave. of both methods = 104.6 ± .4

At first, these results suggested either an improper standard solution of BaO, or an improper factor for BaO in $BaCrO_4$ under the conditions of the precipitation. Assuming the standard to be in error, it was analyzed for BaO by precipitation of the barium as $BaSO_4$, ignited and weighed. This determination yielded results of 99.76 ± .03 mgm/10 ml which shows that the standard solution was not in error, and that in all probability an empirical factor for barium in barium chromate is indicated under the conditions of the precipitation.

At the time of this investigation, the composition of the "sulfate cake" was not known, although there were two possibilities. These two types of cakes will be called "sulfate cake No. I" and "sulfate cake No. II" for convenience. The compositions of these cakes will be approximately the following:

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Table III

Component	Sulfate cake I Ratio	Sulfate cake II Ratio
Barium	1	1
Strontium	1	0.05
Calcium	20	0.2
Lead	100	1
SiO_2	150	1.5

The ratios shown in this table result from probable figures on the process and need not be further clarified. Since calcium, strontium and lead are high in respect to barium in cake No. I, a different separation technique would probably be applied here than in cake No. II, where calcium, strontium and lead are relatively low in respect to barium.

First, separation of equal amounts of calcium, strontium and barium was undertaken. These results are shown in Table IV.

Table IV

mgm BaO added	mgm SrO added	mgm CaO added	mgm BaO Recovered	Remarks
99.8	100	100	114	One precipitation of $BaCrO_4$.
99.8	100	100	109	
99.8	100	100	111	
99.8	100	100	109	
99.8	100	100	104.0	Reprecipitation of the above precipitates.
99.8	100	100	103.6	
99.8	100	100	103.6	

Ave. = 103.7 ± .2

The results of reprecipitating the $BaCrO_4$ are low probably due to a slight loss of barium.

In order to show the separation of calcium from barium in the ratio as shown in cake No. I, a typical sample of the cake, without silica and lead, was analyzed for barium. These results are shown in Table V.

Table V

mgm BaO Introduced	mgm CaO	mgm SrO	mgm BaO Recovered	Remarks
99.8	2,000	100	106.4	Double precipitation of $BaCrO_4$.
99.8	2,000	100	106.8	
99.8	2,000	100	106.9	

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These results are high by only 2% and may be attributed to impurities contained in 4 gms $CaCl_2$ used in preparing the CaO Standard. A blank carried through two precipitations of $BaCrO_4$ showed 3.8 mgm chromate precipitate or 2.3 mgm BaO.

The over-all results shown in tables IV and V present several interesting facts. First, a single precipitation of $BaCrO_4$ is not sufficient to obtain a pure precipitate unless strontium is present in amounts less than 90% of the barium. Second, calcium is easily separated from barium in amounts up 200 times that of the barium. Third, the evidence indicates an empirical factor.

Following the investigation of the separation of barium from calcium and strontium, a sample of a typical "sulfate cake I" containing 100 mgm BaO was analyzed for barium by the whole procedure to determine the reliability. This was unsuccessful for two reasons. 1) The 10 gm PbO contained in the sample (see Table III) could not be quantitatively separated from 2 gm CaO with ammonium acetate. 2) The material left for fusion with Na_2CO_3 was too bulky to be properly fused. These two facts prompted the selection of a sample containing 10 mgm BaO. By performing two ammonium acetate extractions, apparently all the lead and most of the calcium was removed, and a much better fusion resulted. The results of these determinations on 10 mgm BaO are shown in Table VI.

Table VI

Barium Analysis in Artificial AAA Gangue

mgm BaO Introduced	mgm BaO Recovered	Remarks "Sulfate cake I"
9.98	11.6	Single chromate precipitation.
9.98	11.7	Double chromate precipitation.
9.98	11.0	

Ave. = 11.4 ± .3

This data seems to indicate that one chromate precipitation is sufficient to separate the strontium when the preceding separations are carried out. The high results may be explained in part by two means. 1) The blank on the $CaCl_2$ used for CaO is approximately 2%. (See Table V) 2) Lead may be present at the $BaCrO_4$ precipitation step. According to Majdel (7) and Feigl and Weidenfeld (8), $BaPb(SO_4)_2$ may be formed when lead and barium are precipitated together with H_2SO_4. This double salt formation is more prevalent when the ratio of barium to lead is high, and this salt is insoluble in ammonium acetate. Consequently, lead would carry

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through the separation procedure with barium and be precipitated as $PbCrO_4$. Roughly, 1 mgm PbO could account for the error noted in Table VI. This is only 0.1% of the PbO introduced, or 99.9% removal. Majdel shows that in a Pb:Ba ratio 1:0.1, only 94.5% of the lead is recovered (7). The data in this paper seems to support incomplete removal at 1:0.1 ratio.

With this in mind, the proposed procedure was altered to include a reprecipitation of the metal sulfates following the Na_2CO_3 fusion. The $PbSO_4$ was then extracted once with ammonium acetate, the remaining sulfates again fused, and the procedure completed as proposed above. The results of determining barium by this method appear in Table VII.

Table VII

Barium Recovery by the Revised Procedure

mgm BaO Introduced	mgm BaO Recovered	Remarks "Sulfate cake I"
9.98	7.75	
9.98	7.52	Single $BaCrO_4$ precipitation.
9.98	8.35	
9.98	9.38	
	Ave. = 8.30 ± .62	

This data seems to indicate a loss of barium. It may be that in both methods using 10 mgm barium, there is about the same loss of barium, but by the shorter method the loss is compensated for by the precipitation of $PbCrO_4$, while by the longer method, by which lead has presumably been removed, the loss of barium is exposed. Results by the short method are high while the results by the long method are low. The former results are nearer the true value than are the latter.

Summary

A method for determining barium in a sulfate cake composed of large amounts of lead sulfate, calcium sulfate and silica is offered in this paper. This method determines barium gravimetrically by means of a $BaCrO_4$ precipitation following a suitable removal of all the interfering elements. The data in this paper seems to indicate the need of an empirical factor for barium in barium chromate under the conditions of the precipitation. This factor is 4.7% lower than the theoretical factor for barium in barium chromate.

It has been shown in this paper that strontium can be separated completely from barium by a double precipitation of $BaCrO_4$. By precipitating $BaCrO_4$ once, strontium in excess of 90% of the barium content can not be removed. However, it has been shown that in the course of the separation process in a sulfate cake analysis for barium, enough strontium is lost by solubility that one $BaCrO_4$ precipitation is sufficient to separate equal amounts of barium and strontium.

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Large amounts of calcium may be tolerated, as $CaSO_4$ is somewhat soluble in ammonium acetate. Further, it has been demonstrated that large amounts of calcium may be tolerated at the chromate precipitation.

Large amounts of lead may be tolerated within certain limits. It appears impossible to completely separate all the $PbSO_4$ from other sulfates, unless a reprecipitation of all the metal ions as their sulfates is performed. In this case however, loss of barium far exceeds the error due to the presence of the lead.

This paper proposes a sample containing only 10 - 20 mgm BaO. This provides a means of effecting better separations.

In conclusion, the authors feel that this procedure does not entirely satisfy the conditions of an accurate barium determination, for the reason that lead causes a discrepancy which can hardly be avoided under the conditions of the sulfate cake composition. As a result of the interference of trace amounts of lead, the accuracy of this determination can hardly exceed 5%.

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Procedure for Determining Barium in a Sulfate Gangue

This procedure should be run in duplicate.

Select enough of the sulfate cake to obtain approximately 10-20 mgm Ba. Weigh on a torsion balance, transfer to a beaker, adding 20 ml HF and 10 ml H_2SO_4. Digest on a low hot plate until assured most of the silica has been decomposed. Evaporate to dense SO_3 fumes. Cool, dilute to 150 ml and filter on paper, retaining the bulk of the sulfate material in the beaker. Add 50 ml 3N ammonium acetate, heat to boiling and pass through the filter. This should be repeated until the amount of sulfate material is small. Carefully burn off the paper in platinum, add 20 gm Na_2CO_3 and fuse. Dissolve the fusion mass in a minimum amount of hot water and filter. Dissolve the insoluble carbonates with 25 ml 3N HCl, collecting the solution and washings in a 500 ml Erlenmeyer flask. Add 1 drop bromphenol blue, then NH_4OH until faintly blue. The volume at this point should not exceed 50 ml. Add 1 ml 6N acetic acid, 10 ml 3N ammonium acetate and heat nearly to boiling. Add slowly with rapid swirling, 15 ml 10% $K_2Cr_2O_7$. Heat to coagulate the chromate precipitate. (If strontium is present in amounts much over 150% that of the barium, a double $BaCrO_4$ precipitation is recommended.) In the event of a double precipitation, filter the $BaCrO_4$ through a fine sintered glass crucible, retaining the bulk of the precipitate in the flask. Run 10-15 ml cold 3N HCl through the sinter into the original flask to dissolve the precipitate. Slowly add NH_4OH from a pipette with rapid swirling until the solution becomes yellow. Add 10 ml ammonium acetate and heat nearly to boiling. Add slowly 5 ml 10% $K_2Cr_2O_7$ to completely precipitate $BaCrO_4$. Heat to coagulate the $BaCrO_4$, cool and filter in a fine sinter using 1:1 H_2O - C_2H_5OH wash solution. Dry at 110°C and weigh. Calculate as follows:

$$\frac{\text{wt ppt} \times \left(\frac{\text{Ba}}{\text{BaCrO}_4}\right)^{*} \times 100}{\text{wt sample}} = \%\ \text{Ba}$$

$$\frac{\text{wt ppt} \times \left(\frac{\text{BaO}}{\text{BaCrO}_4}\right)^{**} \times 100}{\text{wt sample}} = \%\ \text{BaO}$$

*Theoretical factor = .5421
Empirical factor = .5421 x 95.3% = .5166

**Theoretical factor = .6053
Empirical factor = .6053 x 95.3% = .5769

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