

as given in column 4 gives the soluble arsenic oxid not combined with lead oxid.

The method outlined in this paper gives a rapid and accurate procedure for determining soluble arsenic oxid in commercial lead arsenate. It is pointed out that the solubility of lead arsenate affects the total amount of soluble arsenic oxid and a correction is worked out which gives the amount of soluble arsenic oxid not combined with lead oxid.

NEW HAMPSHIRE
AGRICULTURAL EXPERIMENT STATION,
DURHAM, NEW HAMPSHIRE.

VALUATION OF FLUORSPAR.

By E. BIDTEL.

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In the commercial analysis of fluorspar the determinations usually required are calcium fluoride, silica and calcium carbonate; in some particular cases lead, iron, zinc and sulfur. We have received several calls for percentage of barium sulfate but the most careful qualitative tests have failed to show the presence of this mineral, as will be shown later, in either what is known as Rosiclare or Fairview fluorspar.

There is no practical method for the separation of fluorine from silica and of determining fluorine direct in its ore, which answers the commercial requirements of a mine laboratory. The usual practice followed by most chemists is to determine the total calcium oxide and to calculate from this the amount of calcium fluoride, after deducting the amount equal to the calcium carbonate present, this latter being determined from a separate sample in the usual way by absorbing the liberated carbonic acid in soda-lime tubes. This method would be correct if all the calcium present were combined with either carbonic acid or fluorine and all the carbonic acid present combined with calcium. The first assumption is probably correct as all our experiments go to prove this, but the latter we know is wrong, for lead carbonate, zinc carbonate and iron carbonate are frequently present, especially in the gravel fluorspar. Consequently, the calculated amount for calcium carbonate will be too high and the calcium fluoride in consequence will be too low.

In view of the above error, I have found it better to dissolve all carbonates from the sample by acetic acid, leaving the calcium fluoride and silica as a residue on the filter ready for the determination of both silica and calcium fluoride. It must be remembered that calcium fluoride is slightly soluble in acetic acid. I have reduced this solubility to a factor which I use in my calculations. Generally the amount of calcium carbonate present is greatly in excess of the other carbonates, so that frequently it will be sufficiently accurate for commercial purposes to report the amount soluble in acetic acid after deducting the amount of calcium fluoride soluble in this acid as calcium carbonate. It is to be remembered that at this point there is opportunity for another small error

which, however, is limited, varying with the amount of base metals present; should they be present in considerable quantities the residue must be weighed, after drying at 110° C., to avoid an error caused by their oxidation. Ordinarily, however, this oxidation is so small that it need not be taken into account. In the separation of carbonates and ignition of residue, the loss will also include small amounts of water, volatile and organic matter. The residue left insoluble in acetic acid contains all the silica originally present in the ore. The silica is now determined by volatilizing the same as silicon fluoride. The presence of sulfides of iron, zinc and lead must be considered, and for this reason I have found it best to oxidize the sulfides in the residue by heating with mercuric oxide before evaporating with hydrofluoric acid. In this operation lead sulfide is entirely oxidized to lead sulfate, but the ferruginous zinc sulfide is but slightly acted upon and remains unaffected by hydrofluoric acid, in so far as final results are concerned, as shown by analysis of synthetical samples of known percentages.

In regard to the determination of calcium fluoride, I avoid decomposing the sample and eliminate the calcium fluoride by treating the residue obtained from the silica determination with hydrofluoric acid to transform the iron oxide into iron fluoride and extracting the same together with the lead and zinc by solution of ammonium acetate containing ammonium citrate. The method as used at present follows:

Weigh into a small Erlenmeyer flask one gram of the finely powdered sample, add 10 cc. of ten per cent. acetic acid, cover with a short-stemmed glass funnel and heat on a water bath for one hour, agitating from time to time. Filter through a 7 cm. ashless filter, wash with warm water four times and burn off the filter paper in a weighed platinum crucible at a temperature as low as possible. The loss in weight minus 0.0015 gram (the amount of calcium fluoride soluble in acetic acid under the conditions named) is calcium carbonate.

Add to the residue in the platinum crucible about one gram of yellow mercuric oxide in the form of an emulsion in water; break up any hard lumps that may have formed; evaporate to dryness and heat to a dull red heat; cool and weigh. Add about 2 cc. of hydrofluoric acid and evaporate to dryness, repeating this operation twice, using 1 cc. of hydrofluoric acid in each of the last two operations. Add a few drops of hydrofluoric acid and some macerated filter paper, as recommended by Dittrich, then a few drops of ammonium hydroxide to precipitate the iron and evaporate to dryness. Heat to a dull red heat, cool and weigh; the loss in weight is reported as silica. Now add 2 cc. of hydrofluoric acid and a few drops of nitric acid, cover the crucible with its lid and place on a moderately warm water bath thirty minutes; remove the lid and evaporate to dryness. If the contents of the crucible are not now perfectly white, evaporate again with hydrofluoric acid, add a few drops of hydrofluoric acid and 10 cc. of the solution of ammonium acetate (this ammonium acetate is

prepared as follows: neutralize very carefully 400 cc. of eighty per cent. acetic acid in a liter flask with strong ammonium hydrate; add twenty grams of citric

Average samples of different car loads showed the following percentage, one gram of material being taken for analysis:

		CaSO ₄ obtained by decomposition with H ₂ SO ₄ .			CaF ₂ equal to CaSO ₄ .	Average plus 0.29 per cent.	SiO ₂ .	Soluble in acetic acid less 0.15 per cent.		CO ₂ .	CaCO ₃ equal to CO ₂ .
		Weighed as CaF ₂ .					Average.	Average.			
1	Keystone ground.	99.07	172.75	99.06	99.31	0.44	0.45	0.20	0.24	0.116	0.26
		99.01	172.65	99.01		0.49		0.26			
		99.06	172.63	98.99		0.42		0.27			
2	A-1 Ground	96.81	168.80	96.80	97.09	1.47	1.45	0.88	0.88	0.35	0.80
		96.77	168.73	96.76		1.42		0.90			
		96.86	168.89	96.85		1.45		0.86			
3	Gravel.	89.49	155.72	89.30	89.58	3.31	3.31	4.27	4.23	1.75	3.98
		89.35	155.69	89.28		3.33		4.17			
		89.38	155.71	89.29		3.29		4.25			
4	Gravel.	86.76	151.00	86.59	86.97	4.90	4.93	4.72	4.68	1.95	4.43
		86.87	151.24	86.72		4.93		4.69			
		86.85	151.27	86.75		4.95		4.63			
5	Gravel.	82.14	143.03	82.03	82.32	8.59	8.67	6.09	6.13	2.61	5.98
		82.13	143.00	82.00		8.70		6.18			
		82.08	143.10	82.06		8.71		6.12			
6	Unwashed sand.	66.02	114.80	65.83	66.14	13.76	13.77	15.52	15.58	6.83	15.52
		66.13	114.86	65.87		13.75		15.57			
		66.04	114.82	65.84		13.80		15.65			

acid and fill up to the mark with strong ammonium hydrate). Digest on a boiling water bath for thirty minutes; filter and wash by decantation with hot water containing a small amount of the ammonium acetate solution just described, then with pure, hot water; ignite in the same crucible and weigh. The residue should be perfectly white and should be pure calcium fluoride. To test this, add 2 cc. of sulfuric acid, heat to decompose the calcium fluoride, and evaporate the excess of sulfuric acid; repeat this operation, using 1 cc. of sulfuric acid. Now weigh the calcium sulfate, add five or six grams sodium carbonate, fuse and dissolve in hydrochloric acid in slight excess; should a white precipitate occur at this point it will indicate the presence of barium.

To prove this method I selected clear crystals of fluorspar, pulverized the same and purified it by treating with acetic acid, hydrofluoric acid and ammonium acetate; the washed, dried and ignited powder was decomposed by sulfuric acid and the calcium sulfate weighed. By taking an average of six determinations 0.3875 gram of this fluorspar formed 0.67555 gram of calcium sulfate equal to 99.97 per cent. calcium fluoride. One gram of this fluorspar treated as described showed the following results as an average of twelve determinations:

	Gram.
Loss in weight by treating with acetic acid	0.0015
Loss in weight by treating with HgO and HF	0.0002
Loss in weight by treating with ammonium acetate	0.0012

The amount of calcium fluoride lost in these different manipulations was 0.0029 gram, or 0.29 per cent., if we take one gram for analysis. I now analyzed mixtures of material of known percentage similar in composition to fluorspar and obtained the following results, using one gram for analysis:

	CaF ₂ .	SiO ₂ .	CaCO ₃ .	PbS.	ZnFeS.
Taken	85.11	6.66	5.59	1.50	1.14
Found	85.07	6.61	5.57		
Taken	80.05	7.71	7.92	2.50	1.82
Found	80.03	7.70	7.87		
Taken	78.45	8.32	10.40	1.40	1.43
Found	78.41	8.29	10.34		

The calcium sulfate obtained by decomposition of fluorspar was fused with sodium carbonate and the cake dissolved in hydrochloric acid. The solution was perfectly clear, showing a total decomposition of the fluorspar and the absence of barium.

As our fluorspar does not contain any gypsum and heavy spar, I did not investigate its influence on the calcium fluoride determination, but it is evident that small amounts of calcium sulfate will be leached out, if present, together with the carbonates. Barium sulfate is easy to detect and can be determined as usual.

The only constituent of injurious influence would be any silicate containing calcium. F. Julius Foels, in Bulletin 9 of the Kentucky Geological Survey, states the following silicates occurring associated with Kentucky fluorspar: Apophyllite, Datolite, Desmine, Epidote, Laumontite and Natrolite. Apophyllite and Natrolite cannot be present in the fluorspar because there are no alkalies to detect. The same with Datolite. I could not find any trace of boron; Desmine and Laumontite cannot be present in any considerable amount, there being only very small amounts of aluminum in the spar.

I have made a support of aluminum which enables me to handle six crucibles at a time and I can finish six analyses in ten hours.

LABORATORY FAIRVIEW FLUOR-
SPAR AND LEAD CO.,
GOLCONDA, ILL.

DETERMINATION OF MANGANESE IN STEEL.

By JAMES J. BOYLE.

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After successively trying for some time the color method, Johnson's lead peroxide-sodium arsenite titration method and the ammonium persulphate-sodium arsenite titration method for manganese in steel with varying success, the writer has adopted a suggested