A Comparative Study of Methods for the Determination of Lead in Ores.

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BY

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Before 1862, that the metal was, at least, not of common use among the Indians, and its reduction was probably taught by the white man. Within historic times, however, the use of lead dates back to the earliest records in Asia, Africa, Europe, and America.

In Asia and Africa, lead mines were worked about 1000 B.C., and the metal was used for many different purposes. Lead mining in Europe probably began about the same time along the shores of the Mediterranean and was conducted on a large scale during the Roman period in Spain and Italy and also in France and England. Then the industry languished for a time, but now is carried on quite extensively again. In the United States, the earliest discoveries
of lead appear to have been in Virginia, near Jamestown. Almost all of the great lead ore bodies of the United States are of comparatively recent development, none of those of the far West being generally known forty years ago.

b. Metallurgy.

Lead rarely occurs native, but frequently combined with sulphur as galena ($\text{PbS}$). It is also found as cerussite, white lead ore ($\text{PbCO}_3$); pyromorphite, or green lead ore ($3\text{Pb}_3\text{(SO}_4)_{\text{2}} + \text{PbCl}_2$); mimetite, a lead arseniate ($3\text{Pb}_3\text{(As}_2\text{O}_5\text{)}_{\text{3}} + \text{PbCl}_2$); as anglesite, lead sulphate ($\text{PbSO}_4$); yellow lead ore, lead molybdate ($\text{PbMoO}_4$), and as crocoite, or red lead ore, a lead chromate ($\text{PbCrO}_4$). Of these the galena and the cerussite are the most
common, and lead is obtained almost exclusively from these two. The method for the extraction of lead from its ores in use at most smelting works is in general as follows: If the ore is a sulphide, it is first roasted in the so-called "Continuous Reverberatory Furnace", in order to drive off as much sulphur and arsenic as possible. Carbonate ores, etc., and the roasted sulphide ores are subjected to a reducing smelting in a blast furnace. The charge is made up according to the character of the ore, but in general consists of Coke Ash, Slag, Iron Ore, Limestone and the Lead Ore, and is made up so as to weigh about 1000 pounds. At the bottom of the furnace, the melted masses separate according to their specific gravities, the lead collecting in what is known as the crucible and passing off through
The lead is heated for about four hours and the litharge-like skimming, which has formed, is removed. This operation is repeated once and sometimes twice until the last traces of zinc and antimony are removed. The refined lead is siphoned directly into the moulds and when it has solidified, is chilled with water and trimmed with a sharp chisel-pointed bar. This lead is now ready for the market.
II. Research.

A technical method for the determination of lead in ores, requiring but an ordinary amount of manipulation and occupying a short space of time, has long been desired. A great many have been proposed and, in my work I have tried those, which seem to have met with most success.

There are three general classes of methods: gravimetric, fire assay, and volumetric, and of these I have tried the following on the two most common ores, galena and cerussite, and...
Gravimetric.
1. As Lead Sulphate (\(\text{Pb SO}_4\)).
2. As Metallic Lead (Von Schulz and Lortz).
3. As Lead Chromate (\(\text{Pb Cr}_2\text{O}_7\)).

Fire Assay
4. Charge
   10 grams Ore
   1 Assay Ton Flux
   3 12 Penny Nails
   450 grams \(\text{Na}_2\text{CO}_3\)
   600 grams \(\text{K}_2\text{CO}_3\)
   450 grams Raw Borax
   200 grams Flour

5. Charge - For Galena
   10 grams Ore
   25 grams \(\text{NaNO}_3\)
   10 grams \(\text{K}_2\text{CO}_3\)
   2 12 Penny Nails
   Salt Cover
Charge: For Carbonate Ore.
10 grams Ore.
60 grams KCN.
Salt Cover.

Volumetric:
7. Chromate Method.
8. Knight's Permanganate Method.

In determining the lead as sulphate in the galena, weigh out one gram, add concentrated nitric acid and evaporate to dryness. This will oxidize most of the free sulphur to sulphate. Then add dilute sulphuric acid and alcohol, allow to settle, filter, wash with alcohol, dry, ignite and weigh as lead sulphate. In the case of the carbonate ore, after decomposing
with nitric acid, filter off the silica, add to the filtrate sulphuric acid, evaporate on the water-bath until all the nitric acid is driven off, add alcohol and then proceed as described above. This method is a very good and accurate one, but requires too much time and is therefore not desirable.

Method number 2, proposed by Von Schutz and Law in the Engineering and Mining Journal, consists essentially in forming lead sulphate and precipitating the lead by means of ammonium chloride in the presence of sheet aluminium. Treat one-half to one gram of the ore with ten cc. of nitric acid and five cc. of water. Heat until the ore is decomposed and add ten cc. strong sulphuric acid and heat until nitric acid is expelled.
and the sulphuric is boiling freely. Cool and add ten cc. of dilute sulphuric acid, then two grams of Rochelle salt. When this is dissolved add forty cc. water and heat to boiling. Allow to settle, filter, wash with dilute sulphuric acid. Spread filter out carefully on a watch glass and wash the contents back into the beaker with a stream of boiling hot ammonium chloride solution. Heat until lead sulphate is dissolved, adding more ammonium chloride, if necessary. Again filter and wash with the ammonium chloride solution. Place in filtrate three pieces of sheet aluminium, one sixteenth of an inch thick by five eights of an inch wide and one and three quarter inches long. The aluminium must be pure. Heat to boiling,
remove from heat and shake mixture around to collect the lead. The aluminium should be clean with but little lead adhering. Fill the flask with cold water, invert and discharge the contents into a large casserole and wash there. Remove any particle of lead adhering to the aluminium by rubbing it off under water. Decant and rinse the lead into a small porcelain dish. Then decant as much water as possible and collect and press the lead into a thin sheet with an agate pestle. Wash the lead several times with distilled water and once with alcohol and then dry at a gentle heat. Brush the lead into a watch glass or directly into the scale pan and weigh. The lead is practically free from silver, gold, copper, antimony,
bismuth, etc. This method gives fair results, but it is too easy to make an error in manipulation and it also requires considerable time.

In method number 3, the gravimetric chromate method, get the lead in the form of sulphate as in method number 1. Dissolve off of paper with ammonium acetate and add a little sodium acetate. Heat the solution to boiling and add an excess of a solution of potassium bichromate. Boil, allow to settle, pour off the supernatant liquid, bring precipitate on paper previously dried and weighed and wash well with hot water. Dry at a temperature of about 100°C for about one half hour and weigh. This method is not an accurate one and besides
takes a very long time, so is not at all desirable.

Of the charges used in fire assay, number 4 is by far the best. The others require more time to weigh out and do not give as accurate results. Charge number 4 is one used in most of the smelting works.

Alexander's molybdate method is based upon the fact that ammonium molybdate when added to a hot solution of lead acetate will give a precipitate of molybdate of lead, which is insoluble in acetic acid. Any excess of ammonium molybdate will give a yellow color with a freshly prepared solution of tannin. The tannin solution is made by dissolving one part of tannin in three hundred parts of water. The standard solution of ammonium
molybdate is prepared by dissolving nine grams in one liter of water, and then this is accurately standardized with pure sulphate of lead. Weigh out three hundred milligrams of sulphate of lead and dissolve it in hot ammonium acetate; then acidify with acetic acid and dilute with water up to 250 ce. This is then heated to boiling and then add from a burette the molybdate solution, prepared as above mentioned, until all the lead is precipitated. This is determined by placing the drops of tannin solution upon a porcelain plate, and then add to these other drops from the beaker from time to time. While the lead is in excess, there will be no coloration, but as soon as the molybdate is in excess a yellow color is produced. To determine the lead in
ores, treat from one half to one gram in a porcelain casserole with 15 cc. strong nitric acid and 10 cc. strong sulphuric acid. Heat until all the nitric acid is expelled, then allow it to cool and dilute with cold water, stir and boil until all soluble sulphates are brought into solution. Then filter, leaving as much of the precipitate in the casserole as possible, wash twice with hot dilute sulphuric acid and once with cold water. Next dissolve the sulphate of lead remaining in the casserole with hot ammonium acetate, pour the hot solution on the filter and allow to run into a clean beaker. Repeat this operation until all of the sulphate of lead is dissolved. Wash out the casserole thoroughly with hot water into the filter. Acidify the solution with acetic
acid, dilute up to 250 cc. with hot water. Then heat to boiling and run in from a burette the standardized solution of ammonium molybdate until all of the lead is precipitated. This is an excellent method, as it requires but little time and is very accurate.

For method number 7, the volumetric chromate method, a standard solution of bichromate of potash is made by dissolving 7.13 grams in one liter of water; then one cc. is equal to 0.01 grams lead. Get the lead sulphate as in method number 1, except that the silica need not be filtered off. Dissolve the lead sulphate off of paper with hot solution of acetate of soda, dilute to about 150 or 200 cc. and run in standard solution of bichromate. The end reaction
is determined by bringing a drop of the solution in contact with a drop of neutral silver nitrate solution on a porcelain plate. A red coloration shows excess of bichromate. Formerly this method was used very much, is however not as accurate and easy to carry out as Alexander's molybdate method. The greatest objection to be brought against it is the uncertainty of the complete precipitation of the lead as the chromate, if special precautions are not observed, the length of time involved in the process, and finally the ease with which the end point of the reaction can be overstepped.

Knights permanganate method is based on the formation of oxalate of lead, the
decomposition of this salt by sulphuric acid, the determination of the liberated oxalic acid by permanganate of potassium solution and the calculation of the lead percentage from the amount of oxalic acid with which it was originally combined. The standard of the permanganate being established, weigh out a portion dissolve in three cc. concentrated nitric acid, dilute with ten cc. hot water and add carbonate of sodium in slight excess. Dissolve the precipitate by adding five cc. strong acetic acid, and then add twenty cc. of ninety-five per cent alcohol. Heat to 65°C. and precipitate the lead by adding ten cc. of a saturated solution of oxalic acid; after settling, filter the precipitate and wash thoroughly
with hot water. Now rinse the lead oxalate from the filter into a beaker and add fifty cc. of hot water and five cc. concentrated sulphuric acid. Warm the solution to about 65°C. and titrate the free oxalic acid. This method, while a very fair one, is not as good as Alexander's.

All of these methods described, I have given numerous trials, selecting and tabulating results for the purpose of comparison. From this table, it can be seen that in both ores, the highest results were obtained by means of Alexander's method. The duplicates also agreed well in this method. Of all of the methods, then, proposed for the
determination of lead in ore, Alexander's molybdate method, the most recent of all, seems to be the best, as it does not require much time, is easy to carry out and is accurate. This method may be somewhat shortened by throwing the filter paper, through which the soluble sulphates have passed, directly into the casserole containing the sulphate of lead precipitate. Then add the hot ammonium acetate and digest for a few minutes to insure complete solution of the lead sulphate; acidify this solution with acetic acid and dilute up to 250 cc. as before, with hot water, next heat to boiling and titrate as before. This is not quite as neat and accurate, but takes less
time. It may be made perhaps more satis-
factory by using a hardened filter and
washing the residue back in the caserole.
Another advantage of Alexander's method
is the fact that arsenic, antimony and
phosphorus do not interfere, as they
readily pass through the filter in solution.
<table>
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<tr>
<th>Method</th>
<th>Ore Taken</th>
<th>Weight Precipitate</th>
<th>Weight of Lead</th>
<th>Per Cent of Lead</th>
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<tbody>
<tr>
<td>1</td>
<td>1 gram</td>
<td>1.2456</td>
<td>.8509</td>
<td>85.09</td>
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<tr>
<td>2</td>
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<td>1.2885</td>
<td>.8245</td>
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<td>7</td>
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<td>84.70</td>
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<td>8</td>
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<td>.4238</td>
<td>84.76</td>
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## Carbonate Ore

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<th>Weight of Lead</th>
<th>Per Cent of Lead</th>
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<td>.44 22</td>
<td>.30 209</td>
<td>30.21</td>
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<tr>
<td>2</td>
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<td></td>
<td>.2872</td>
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<tr>
<td>3</td>
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<td>.28 08</td>
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<tr>
<td>8</td>
<td>.5 gram</td>
<td>11.4</td>
<td>.14 82</td>
<td>29.64</td>
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