ature told of a stable zinc-thallium alloy. The very first attempt to use a zinc-thallium amalgam was successful. The amalgam was repeatedly washed and the water gave no precipitate with potassium iodide. Several other metals were tried as substitutes for zinc. These were Ni, Ag, Mg, Ba, Ca, Cr, and Cd, but the results were not satisfactory except with cadmium. The thallium amalgams with zinc and cadmium are not only stable towards water but it is possible to wash them with alcohol and ether without solution of the thallium, so that the usual rapid method of drying the electrolytic amalgam may be followed.

The procedure adopted in the determination of thallium by means of the mercury cathode, therefore, resolved itself into (1) the formation of a dilute zinc amalgam by electrolysis of a zinc sulphate solution in the ordinary mercury cup, and (2) the use of the zinc amalgam thus obtained as the cathode for the deposition of thallium.

The following table gives results obtained by this method:

	Tl_2SO_4, cc.	H_2SO_4, cc.	Time, min.	Current.		Weight, gm.
				Amp.	Volt.	
1	10	10	7	5	11	0.1124
2	10	7	7	5	11	0.1120
3	10	7	7	5	11	0.1124
4	10	7	7	5	11	0.1125
5	10	7	10	5	11	0.2254
6	10	7	10	5	11	0.2252
7	10	7	10	5	11	0.2250

Similar results were obtained with a cadmium-thallium amalgam.

From a series of experiments made to ascertain the minimum quantity of zinc necessary to prevent oxidation of the thallium it was found that with so small a quantity as 0.0007 g. of zinc present the wash water was free from thallium when the amalgam contained 0.1142 g. of the latter metal.

From the foregoing it will be seen that the electrolytic determination of thallium can be quickly accomplished by the use of a mercury cathode and rotating anode.

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AN APPLICATION OF GRADED POTENTIALS TO ORE ANALYSIS.

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An ore was sent in recently to this laboratory for analysis, its content in lead, silver and copper being desired.

A qualitative analysis showed large amounts of lead, less of silver and copper, together with iron, magnesium, aluminum and calcium. The mineral was a carbonate.

The ore was evidently high in lead and low in the other constituents.

It was decided to try the method of constant potential for the determination of the lead, silver and copper, endeavoring to use the simplest working conditions and only such apparatus as is to be found in any ordinarily equipped laboratory.

The method proposed was to deposit the silver on the cathode and the lead as peroxide on the anode, using a nitric acid solution of the ore. After the deposition of the lead and silver, the e. m. f. would be raised sufficiently to deposit the copper. These three elements were all that it was desired to determine.

The electrolytic cell consisted of a 45-gram platinum crucible with a smaller concentric one of about 16 g. weight supported by a device made of a thread spool on the end of a wooden rod and contacts of thin copper strips secured in the lower end of the spool and pressing against the inner walls of the crucible holding it in place and making electrical connection with the solution.

The space between the two crucibles at the top was about five millimeters and the capacity of the inner concentric space about 30 cc. In each analysis 25 cc. of the solution were used.

It was found that current flowed through a silver nitrate solution at 0.9 volt and with copper nitrate at 1.6 volts, thus giving a wide enough margin for practical purposes and ordinary manipulation.

The current was obtained from a large storage battery. As resistances a spare rheostat of the ordinary type was used as a variable in series with a fixed set of spools on the switchboard. The solution was connected as a shunt on the sliding rheostat. The voltmeter was an ordinary Weston instrument reading up to 15 volts in 0.2 volt divisions. The potential could be nearly enough adjusted to 0.05 volt.

A few qualitative electrolyses were made in order to determine the effect of acid concentrations. A solution with 18 per cent. free nitric acid gave a good anode deposit but no cathode deposition.

With 3 per cent. free HNO_3 a good deposit at the cathode was obtained but no lead peroxide at the anode. Concentrations of 10 and 12 per cent. free nitric acid gave unsatisfactory results as regarded the lead, which was not all deposited.

With 14 per cent. of free nitric acid and a weight of ore of 0.2102 gram in 25 cc. of solution a complete precipitation of the lead was obtained. The time factor in this instance was too protracted for commercial needs and a change of conditions was sought for.

Fourteen per cent. of free acid was shown to be the maximum limit for successful deposition of the silver as this rapidly dissolved from the cathode when the potential fell to 1.2 volts.

This shows that at 1.4 volts and 14 per cent. acid the silver is nearly as rapidly dissolved as deposited and the equilibrium point is nearly reached. In a separate experiment to determine the rate of deposition of the silver it was found that at 1.4 volts very complete deposition of the silver had occurred.

The fact was also noted that after the anode had been wholly coated with the peroxide layer further deposition occurred more rapidly, *e. g.*, in one-half hour 0.0038 gram of lead peroxide was deposited, while in an hour the deposit was 0.0162.

In the procedure next employed the silver was deposited in about 2 hours at 1.4 volts potential. After its removal in this manner from the solution the lead and copper were obtained at 2 volts, in about 15 hours. Six per cent. of free nitric acid was found to be insufficient for complete deposition of the lead, owing to cathodic reduction. With 12 per cent. of free nitric acid and the above procedure, concordant results were obtained.

The composition of the ore in lead, silver and copper was found to be silver 1.15, copper 1.14, and lead 52.3 per cent.

The experimental results may be summed up in the form of a procedure. Two grams of the ore are dissolved in nitric acid and any free acid neutralized. Next there is added 30 cc. of nitric acid of 1.42 specific gravity.

The solution is then diluted to 250 cc. and 25 cc. of this are taken for analysis. With an e. m. f. of 1.4 volts the silver is removed in 2 hours and after rinsing, drying and weighing the silver the electrolysis is continued at 2 volts over night.

The next morning the solution is removed and the copper and lead dioxide washed, dried and weighed. It is advisable to dry the lead peroxide at 160°–180°, raising the heat slowly, and keeping at the higher point for 1/2 hour, to an hour, depending on the weight of peroxide. During the last half hour of the silver deposition the potential must be carefully kept at 1.4 volts to avoid re-solution of the silver by the nitric acid present. A similar precaution is necessary in the deposition of the lead and copper. If the voltage goes much over 2 volts the acid begins to be electrolyzed and hydrogen is evolved that rapidly destroys the free acid and causes low lead value, owing to incomplete formation of the peroxide. In one experiment the voltage accidentally rose to 2.5 volts. The solution became strongly ammoniacal and the percentage of lead peroxide was very low.

An interesting fact in connection with the silver was noticed. This lay in the observance that no silver peroxide was formed on the anode. It is commonly necessary to add oxalic acid in silver separation from nitric acid to avoid this peroxide formation. In this case the non-formation is probably due to the small amount of silver present.

Several determinations by the above procedure gave Ag 1.12. 1.19, 1.15; Cu 1.14, 1.18, 1.11; Pb 52.36, 52.21, 52.29.

The time factor is satisfactory on considering that three elements are determined in something over 15 hours, with a minimum of attention, and very simple apparatus.

It appears from the experience here given that the method of constant potential separation can be simply applied in commercial analyses when the voltage margin is not too narrow.

By arranging to stir the solution and employing larger surfaces for deposition the time factor can be reduced, but this complicates the apparatus.

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NOTES.

On the Gravimetric Determination of Zinc as Pyrophosphate.—In the original method, Tamm[1] used disodium phosphate as precipitant, adding a large excess to the slightly acid solution containing zinc and excess of ammonium chloride. Later, Dakin[2] used ammonium phosphate, and washed the precipitate with a 1 per cent. solution of it, finally washing with 95 per cent. alcohol.

In order to determine whether ammonium phosphate is superior to sodium phosphate as precipitant, and whether water could be used for washing as well as ammonium phosphate solution, a few experiments were made as follows:

To the hot solution containing the zinc as sulphate in a Jena beaker, was added ten times as much ammonium phosphate in 10 per cent. solution as there was zinc present (total vol. 150 cc.). The precipitate was allowed to settle on the steam bath until small in bulk (required about 30 mins.), and filtered on a porcelain gooch crucible, washed five times with cold water, and ignited to constant weight over a Bunsen burner.

Grams zinc taken: 0.2240, 0.1841. Found: 0.2242, 0.2242, 0.2242, 0.1839, 0.1844, 0.1841.

The above procedure was repeated, but to the zinc solution before precipitating were added 10 cc. of 30 per cent. acetic acid, 20 cc. of nitric acid (1 cc. = 0.47 g. HNO_3), and the solution made neutral to litmus with ammonium hydroxide. If an excess of ammonia is present, it either keeps some zinc in solution, or if evaporated off, causes the precipitate to adhere firmly to the glass.

Grams zinc taken: 0.1841. Found: 0.1847, 0.1836, 0.1836, 0.1836, 0.1839.

The first procedure was next varied by washing with 1 per cent. ammonium phosphate and 95 per cent. alcohol.

Grams zinc taken: 0.2240. Found: 0.2250, 0.2245, 0.2242.

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[1] *Chem. News*, **24**, 148.

[2] *Z. anal. Chem.* **39**, 273.