

to tripotassium nitrophenoldisulphonate. A residue containing 60 parts nitrogen per million gave similar results.

In a third paper the authors will discuss the phenolsulphonic acid method as applied in practice with special reference to sources of error.

### Summary.

The yellow color of alkaline solutions of nitrate containing water residues treated with standard phenolsulphonic acid reagent is due to the tripotassium salt of nitrophenoldisulphonic acid, this salt having been isolated and its properties studied.

No other compound giving a yellow color with alkalis could be isolated or detected in appreciable amount, in treated water residues containing from less than 1 to 60 parts per million of nitrogen as nitrate.

In water residues containing over 50 parts per million nitrogen as nitrates traces of picric acid detectable by microchemical methods may be formed in the cold, but traces only.

Water residues heated in contact with phenoldisulphonic acid yield traces of picric acid, but only traces, unless the heating is long continued and the quantity of nitrate high, when appreciable amounts of picric acid may be formed.

Alkali salts of phenoldisulphonic acid occlude sufficiently large amounts of the alkali salts of nitrophenoldisulphonic acid to so color them and so modify their crystal form as to simulate in appearance and behavior another nitro compound.

CORNELL UNIVERSITY CHEMICAL LABORATORY.

---

[CONTRIBUTION FROM THE LABORATORY OF DR. HERBERT M. HILL, BUFFALO, N. Y.]

## THE MERCURY CATHODE IN RAPID ELECTROANALYSIS.

BY W. S. KIMLEY.

Received October 8, 1909.

Mercury is superior to platinum for a cathode in several electroanalytical determinations; in some others there is no decided choice, and in several others there is no substitute for the platinum cathode. Some metals can be determined by using a mercury cathode, in an electrolyte that would not give a quantitative deposit on platinum in that the metal seems to be withdrawn from the solvent action of the electrolyte to a certain extent, *e. g.*, copper may be deposited from a solution containing 10 per cent. of nitric acid to within 0.05 per cent. by use of a mercury cathode, while with platinum it would be difficult to recover over 98-99 per cent. With some other metals mercury is superior because it will amalgamate with metals that would not always adhere well to platinum.

The method of H. Filippo,<sup>1</sup> in which the method of Kollock and Smith

<sup>1</sup> Leiden Univ., *Chem. Weekblad*, 6, 2269.

is modified to obviate working with small volumes, is to place an accurately weighed quantity of mercury in a round-bottomed flask, into the bottom of which is fused a platinum wire which barely projects through the glass and makes connection with the mercury.

When the electrolysis is finished the amalgam is washed with water and alcohol and is poured into a weighing bottle half filled with alcohol. The alcohol is then removed with a pipette and a strip of blotting paper and the mercury is dried and weighed.

This method is open to criticism for several reasons. First, the end of the wire would closely hold a small drop of the amalgam and give low results. Second, although clean mercury can be easily transferred from one dish to another without loss, it would be difficult with many of the amalgams. Mercury loses some of its physical properties when it is alloyed with other metals. The meniscus loses its characteristic convex shape and even becomes concave in some instances.

The following method, originated by the author, is easy of accurate manipulation and will give satisfactory results with those metals to which the mercury cathode is adapted, and it also avoids working with the small volume used by Kollock and Smith. A platinum wire is sealed into the bottom of a round-bottomed fat flask weighing about 25 grams and holding about 125 cc.; 40 grams of mercury will cover the bottom of the flask and the outfit will weigh about 65 grams. When the deposition is complete the solution is siphoned off as far as possible without breaking the circuit, the flask filled with distilled water, and this repeated until the current drops nearly to zero. The flask is then removed from the stirrer and the liquid removed by a glass tube drawn out to a point like the tip of a wash-bottle, and attached to the suction pipe of a filter pump by a rubber tube. When the liquid is nearly all out, the flask is slightly tipped and a bare spot will appear where the tip can be placed against the glass and the last drop of water removed. By this method over 98.5 per cent. of the liquid can be easily withdrawn. After thoroughly washing with water, wash three times with alcohol, removing it in the same way except that it is caught in an empty wash-bottle and distilled over quicklime, when a sufficient quantity has accumulated. The amalgam is then washed once with ether and dried in a hot water oven until there is no odor of ether or alcohol, the flask being removed at intervals of one minute and the vapor blown out.

When it is easy to keep the volume small a convenient cell for the electrolysis can be easily made by placing the mercury in a common straight-sided weighing bottle holding about 60 cc. and making the connection by a platinum wire sealed in a glass tube reaching to the bottom and bent at the top so it nearly touches about half way up (Fig. 1). This keeps the tube at one side of the dish so that it does not interfere with the

stirrer. The amalgam is washed and dried as before. In making the tube for connecting with the mercury, the wire is sealed in one end of the tube and the tube is then bent into shape and the other end is sealed so that no moisture may gather in the tube.

In using the above cells they should be washed and dried the same before electrolysis as after, to obtain two weights under the same conditions.

The method of connecting with the mercury cathode through the glass tube is not considered superior to sealing a wire in the bottom of the weighing bottle, but it is easily prepared and avoids breaking an expensive piece of apparatus in some subsequent heating or cooling. The same method might be conveniently adapted to connect with the mercury in the round-bottomed cathode chamber (Fig. 2).

Because some of the metals exert a certain influence on others when they are present together, the following experiments were made on the determination of mixtures made by weighing out portions of chemically pure metals and dissolving them together.

A mixture containing, copper 85, lead 5, zinc 5, and tin 5 per cent., was dissolved in nitric acid (sp. gr. 1.20), evaporated nearly dry, diluted with water, boiled, allowed to stand a few minutes, and the precipitate, containing the tin and small amounts of copper and lead, was filtered off and fused with equal parts of sodium carbonate and sulphur in a small covered porcelain crucible. The fused mass was then dissolved in hot water and enough sodium sulphite added to reduce the polysulphides and so render the copper and lead sulphides insoluble. The tin in solution was filtered off and the insoluble sulphides dissolved in nitric acid and returned to the first filtrate, which measured less than 100 cc. This was then placed in the first described cathode chamber, previously prepared and weighed. The anode was of the disc form and was also weighed before attaching to the rotator. The anode was run very slowly to avoid detaching any of the lead peroxide. After starting the rotator the current was turned on and 15 cc. of nitric acid added. The lead separated on the anode and after washing with water, alcohol, and ether, was dried for 1.5 hours at 190° and weighed as peroxide.

The copper separated and formed an amalgam, and after washing and drying the gain in weight of the cathode chamber gave the weight of the copper.

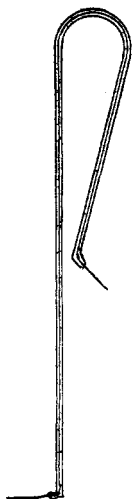


Fig. 1.

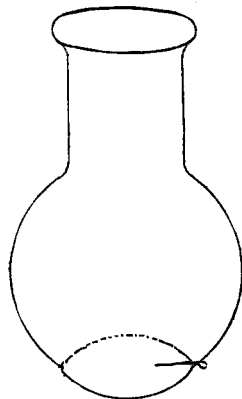


Fig. 2.

The solution and washings from the determination of lead and copper were run into a casserole, 0.5 cc. of sulphuric acid added and evaporated to fumes to drive off the nitric acid. The residue was then dissolved in a small amount of water and a few drops of sulphuric acid, if necessary. The acid was then neutralized with ammonia and an excess of 0.2 cc. of sulphuric acid added, then placed in the mercury cathode chamber made from the weighing bottle and electrolyzed for zinc. To the solution containing the tin was added 5 cc. of strong sodium hydroxide, 10 cc. of concentrated sodium sulphide solution and 20 grams of ammonium sulphate. It was then digested on the water bath for an hour and the tin deposited, using a platinum dish as a cathode, small amounts of ammonium sulphide being added as necessary to keep the sulphides in solution.

The accompanying table gives some of the results:

Constituent.	Voltage.	Amperes.	Time. Min.	Amount of metal present. Per cent.	Amount of metal found. Per cent.	Per cent. error.
Copper.....	5	2	120	85.00	84.98	-0.02
Lead.....	5	2	120	5.00	5.04	+0.04
Zinc.....	10	2	90	5.00	5.00	0.00
Tin.....	6½	2½	120	5.00	4.97	-0.03
Total,					99.99	
Copper.....	5	2½	120	85.00	84.97	-0.03
Lead.....	5	2½	120	5.00	5.03	+0.03
Zinc.....	10	2	45	5.00	5.01	-0.01
Tin.....	6½	2½	180	5.00	4.97	-0.03
Total,					99.98	

In the two following experiments the copper was deposited on platinum foil, other conditions remaining the same.

In the first one, 15.82 per cent. of copper was precipitated on the foil in 120 min., leaving 69.18 per cent. of copper not recovered, and in the second one 18.09 per cent. of copper was precipitated in 150 min., leaving 66.91 per cent. not recovered.

The solutions containing the remainder of the copper were each neutralized with ammonia, made just slightly acid with nitric acid and 0.2 cc. of sulphuric acid added, and the rest of the copper was recovered to within an error of 0.03 per cent. in the first and 0.07 per cent. in the second.

The above does not show that mercury is superior to platinum for the determination of copper, but it indicates that it is better when copper must be determined from a strongly acid solution, as is the case when the separation from lead is made; otherwise the gauze or foil is handier, as it is easier to wash and dry.

To illustrate the working of the process, the results of the analysis of two commercial alloys are given. The copper and zinc were deposited in mercury, the copper in the cathode chamber made from the round-bottomed flask and the zinc in one made from a straight-sided bottle. The results in No. 1 were checked by another chemist who got practically the same results, and in the case of the zinc exactly the same.

	No. 1. Per cent.	No. 2. Per cent.
Copper.....	81.18	83.72
Lead.....	4.76	5.34
Zinc.....	10.04	8.61
Tin.....	3.40	2.43
Iron.....	0.63	....
	<hr/>	<hr/>
	100.01	100.10

It has been stated by Price, *Journal of the Society of Chemical Industry*, that a mercury cathode gives low results with zinc on account of small particles of the amalgam being detached and lost during the process of washing, but by the above method of washing and drying there is apparently no loss, as in nearly every determination on known amounts of zinc the weight of the amalgam indicates at least the whole amount of zinc and in many instances from one- to three-tenths of a milligram more, which is probably due to a slight oxidation of the zinc while drying. Zinc is one of the metals that is best determined as an amalgam, for when deposited on platinum it is difficult to remove without rendering the platinum black and spongy.

Trials with antimony were unsuccessful, as the antimony formed on the surface of the mercury as a black powder and some became lost in washing.

Tin in solution as sulphate forms an amalgam but as yet has given low results.

Several mixtures were made by dissolving copper 0.50, lead 0.35, zinc 0.10 and tin 0.05 gram, and analyzed the same as before, except that the bulk of the lead was precipitated as sulphate and filtered on a Gooch and weighed as sulphate. The small amount remaining was electrolyzed and weighed as lead peroxide and the two added together. This has been found by numerous experiments to give the best results when dealing with comparatively large amounts of lead, as if all the lead is deposited as peroxide the results will be high.

In these mixtures of metals the largest percentage error was 0.04 per cent.

The above described mercury cathode chambers have been placed in the hands of inexperienced persons for the determination of copper, nickel, and zinc, and after a few trials they have been able to get results equally as accurate as the ones recorded above.