

The titration of sulfate solutions which were saturated with sodium chloride was best carried out in 50 per cent alcohol. The total volume was kept to 30 to 40 ml. The following procedure for the indicator spot was found to be more satisfactory in this case. A drop of the indicator solution was placed near a drop of 15 to 20 per cent silver nitrate, so that the spreading boundaries just met. The drop from the titration flask was put inside the silver nitrate spot, close to the indicator spot, and the color change was observed at the boundary. A second silver nitrate spot-indicator spot pair was used as a control.

Use of Spectrophotometer in Confirmation of the End Point

Qualitative absorption curves of the sodium salt of tetrahydroxyquinone in 50 per cent alcohol (in such concentration that maximum absorption in 2-cm. cuvettes was approximately 50 per cent) and of the barium salt were run (Figure 1). It is clear from the curves that the optimum wave length for the detection of the end-point color change is about 525 μ . Accordingly, the end point was checked with the aid of a Coleman Universal spectrophotometer.

The spectrophotometer wave-length dial was set at 525 μ , and the per cent transmission of the indicator solution was de-

termined. The titration was then carried out in the manner described above. When a drop was taken from the titration flask just prior to the end point and added to the cuvette, no change in the per cent transmission occurred. However, a drop of the end-point solution lowered the per cent transmission from 52 to 45. This method could be used for confirmatory purposes only, for the addition of pre-end point solution to the cuvette would build up a sulfate-ion concentration and lead to a false value.

Summary

A method of using tetrahydroxyquinone as an outside indicator in the determination of sulfate is described, which can be conveniently and rapidly used, and with considerable accuracy. It offers a means of removing interfering substances such as aluminum ion and a large excess of sodium chloride. The possibility of using a spectrophotometer in confirming the end point in this titration is pointed out.

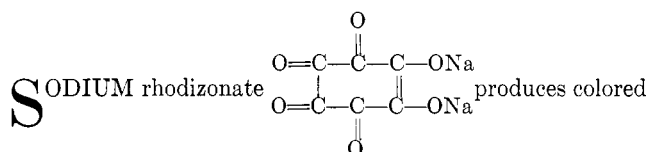
Literature Cited

- (1) Brunjes, H. L., and Manning, M. J., *IND. ENG. CHEM., ANAL. ED.*, 12, 718 (1940).
- (2) Mahoney, J. F., and Michell, J. H., *Ibid.*, 14, 97-8 (1942).
- (3) Peabody, W. A., and Fisher, R. S., *Ibid.*, 10, 651 (1938).
- (4) Zararov, G. V., *Zavodskaya Lab.*, 8, 933-5 (1939).

Analytical Use of Sodium Rhodizonate¹

FRITZ FEIGL AND HANS A. SUTER

Ministerio da Agricultura, Laboratorio Central da Produção Mineral, Rio de Janeiro, Brazil



precipitates when added to solutions of barium or strontium salts. Feigl (2) was the first to apply this fact as a basis for spot tests for barium and strontium. Barium rhodizonate is stable toward acetic acid and dilute hydrochloric acid but is decomposed by sulfate ion, and accordingly Gutzeit (5) used it in his spot-test method of detecting sulfate. The formation and decomposition of barium rhodizonate have also made it possible to use sodium rhodizonate as indicator in the volumetric determination of barium or sulfate. A considerable number of papers have dealt with this method of determining the equivalence point of the sulfate-barium reaction (1, 4, 6, 8, 9, 10).

This laboratory has been studying the possibilities of further analytical uses of sodium rhodizonate and the behavior of this reagent toward various metal ions has been examined. It has been found that this salt exhibits a selective action. With certain univalent and divalent metal ions it forms colored precipitates, whereas it produces no visible reaction with trivalent or quadrivalent cations. Bismuth is an exception, presumably because it can function in its salts as the bismuthyl radical, BiO^+ .

Table I exhibits the findings obtained with 1 per cent neutral and acidified salt solutions. The behavior of the respective hydroxides and oxides is also recorded.

The behavior of iron salts is to be noted. Fe^{++} salts in neutral solution form a red-brown precipitate, which quickly becomes black-blue, probably through oxidation. In solutions of pH 2.8 there is no reaction. Fe^{+++} salts form no precipitate but produce a blue-green color; rhodizonic acid is a phenol and therefore reacts with Fe^{+++} salts like other phenols. In the presence of fluoride no color reaction occurs, owing to the formation of the complex FeF_6^{---} ion.

In the presence of fluoride ion the behavior of Fe^{++} salts is remarkable. The yellow of the rhodizonate solution is immediately discharged. No explanation can be given for this phenomenon, though it may be due to the increase of the reduction potential of Fe^{++} salts in the presence of fluoride ion, so that the oxidation of rhodizonic acid is induced by autoxidation of Fe^{++} salt.

From the analytical viewpoint, the formation of the slightly soluble red and blue-violet lead rhodizonates is particularly interesting. Under certain well-defined conditions, specified below, these precipitates can be utilized as a sure test for lead. These new tests are so sensitive that positive results are immediately given by even such slightly soluble materials as lead sulfide, lead sulfate, lead chromate, alloys, and a wide variety of other lead-bearing materials.

Rhodizonic acid can be used only as its sodium salt. This is a black-green solid; its water solutions are orange to yellow, depending on the concentration, and are stable for only a few days, even if stored in a refrigerator. The color changes and finally disappears, owing to a gradual decomposition arising from the ease with which rhodizonic acid is oxidized to

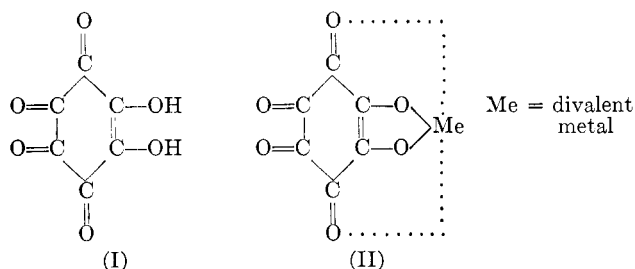
TABLE I. REACTIONS WITH SODIUM RHODIZONATE

Metal Ion	Metal Salt Solution Neutral	Solution pH = 2.8	Hydroxide	Oxide
Ag^+	Black	Black
Hg^+	Brown-red	Brown-red	(disappears on standing)
Ti^+	Dark brown	Dark brown
Pb^{++}	Blue-violet	Scarlet	Blue-violet	Blue-violet
Cu^{++}	Orange-red
Hg^{++}	Red-orange
Cd^{++}	Brown-red	Brown-red	Gray-brown
Bi^{+++}	Brown-red	Brown-red
Ni^{++}
Co^{++}
Zn^{++}	Brown-violet	Brown-violet	Brown-violet
Mn^{++}
FeO_2^{++}	Brown
Be^{++}
Mg^{++}
Ca^{++}
Ba^{++}	Red-brown	Red-brown	Brown-red	Brown-red
Sr^{++}	Red-brown	Red-brown	Red-brown
Sn^{++}	Violet	Violet
Sn^{++++}
Al^{+++}
Zr^{++++}

¹ Translated by Ralph E. Oesper, University of Cincinnati.

croconic and leuconic acids. The decomposition of sodium rhodizonate is hastened by ultraviolet light, particularly if the salt is finely divided in the capillaries of paper.

The intense color of all water-insoluble rhodizonates and also of the soluble alkali salts in the solid state is worthy of consideration, as it indicates that these compounds may be inner-complex salts. This conception is justified. In rhodizonic acid (I) the two acid hydrogen atoms are so situated with respect to the adjacent CO-groups, which are capable of developing auxiliary valences, that the 5-membered rings, characteristic of inner-complex salts, can form. Accordingly, the inner-complex salts of rhodizonic acid can be formulated as shown in (II):



The two rhodizonates of barium, and the two lead rhodizonates that have been isolated and are described below, are basic salts. It may well be that the color of these four compounds is likewise due to inner-complex rings of the type pictured above.

Preparation of Lead Salts of Rhodizonic Acid

Two rhodizonates, each with a distinctive color, can be precipitated from lead solutions by sodium rhodizonate. A blue-violet amorphous precipitate is thrown down from neutral lead solutions; whereas a crystalline, scarlet-red product is precipitated from weakly acidified lead solutions. Digestion with a dilute acid transforms the amorphous form into the crystalline.

BLUE-VIOLET LEAD RHODIZONATE, $PbC_6O_6 \cdot Pb(OH)_2 \cdot H_2O$. Solutions containing 0.825 gram of lead nitrate and 0.55 gram of sodium rhodizonate, respectively, are mixed, brought to boiling and filtered, and the precipitate is washed with water and dried at 105° C. Weighed samples of the dried product were fumed several times with concentrated nitric acid, the residue ignited gently, and then taken to dryness with concentrated sulfuric acid. The resulting lead sulfate was weighed. An average lead content of 65.24 per cent was found; this agrees well with 65.3 per cent demanded by the formula $PbC_6O_6 \cdot Pb(OH)_2 \cdot H_2O$.

A basic lead rhodizonate corresponding to the formula $PbC_6O_6 \cdot Pb(OH)_2 \cdot 5H_2O$ is obtained if the product precipitated by the foregoing procedure is not heated, but instead is freed of moisture by successive treatments with alcohol and ether. The calculated lead content is 58.64 per cent; found, 58.30 per cent.

SCARLET-RED LEAD RHODIZONATE, $2Pb(C_6O_6) \cdot Pb(OH)_2 \cdot H_2O$. Lead nitrate solution (1 per cent) was treated with an excess of buffer solution and heated to boiling, and any lead tartrate that had precipitated was removed by filtration. The buffer solution (pH = 2.79) contained 15 grams of tartaric acid and 19 grams of sodium bitartrate per liter (?). A saturated solution of sodium rhodizonate was added to the clear filtrate; the resulting red precipitate was washed free of excess lead with water, and then dried at 105° C. Analysis showed the compound to contain 61.69 per cent lead; the foregoing formula demands 61.60 per cent.

Analytical Uses of Sodium Rhodizonate

This laboratory has made a study of the use of sodium rhodizonate for spot-test analysis. This reagent can now be recommended for detection of (1) barium; (2) strontium; (3) barium in the presence of strontium; (4) strontium in the presence of barium; (5) sulfate; (6) barium and strontium in the carbonate precipitate of the alkaline earth metals;

(7) lead in dilute solutions; (8) lead in the presence of ions that otherwise interfere; (9) lead in ores and minerals; (10) lead in alloys; (11) lead in pigments, glass, etc.

Cases 1 to 5 have been discussed elsewhere (3). Accordingly, only the newer possibilities of using sodium rhodizonate are described here.

Detection of Barium and Strontium in Carbonate Precipitate of Alkaline Earth Metals

Barium carbonate is more soluble than calcium or strontium carbonate and if it is thoroughly washed and then spot-tested directly with sodium rhodizonate a brown-red precipitate appears. Calcium and strontium carbonate do not react under these conditions. However, this differential behavior cannot be used indiscriminately to detect barium in a mixed carbonate precipitate, because barium rhodizonate is formed only if a very large excess of barium carbonate is present. When a mixture of the carbonates is thrown down, the barium carbonate may be enveloped by calcium or strontium carbonate, and thus shielded from the action of the sodium rhodizonate.

The alkaline earth metals are precipitated together as carbonates by the addition of ammonium carbonate to the solution obtained in the course of the usual qualitative scheme of analysis. To detect barium, or strontium, or both in this precipitate it suffices to place about 1 mg. of the thoroughly washed precipitate in the depression of a spot plate, add one drop of 0.2 per cent solution of sodium rhodizonate, and stir. If a positive reaction is obtained barium is present. If no reaction is observed, it is acidified with one drop of 1 N acetic acid. A red precipitate or coloration will indicate the presence of barium, strontium or both.

Detection of Lead

The formation of either the blue-violet or the scarlet-red lead rhodizonate can be used to detect lead. When testing for lead in neutral solutions that contain no other significant solutes, the conditions should be so chosen that the blue-violet salt is formed. Insoluble compounds should be treated directly with the tartaric acid-bitartrate buffer solution, whose composition has been stated above, because it also serves to dissolve sufficient lead to give the test.

IN SOLUTIONS. A drop of the test solution is placed on filter paper. After the solution has been soaked up, the spot is touched with a drop of 0.2 per cent solution of sodium rhodizonate. A blue-violet fleck or ring is formed if lead is present. Identification limit: 0.1 microgram of lead; concentration limit: 1 to 500,000.

The lead in extremely dilute solutions can be concentrated by the following procedure:

Ten milliliters of the test solution are treated with 1 ml. of 0.2 N mercuric chloride, the mixture acidified, and the mercury, together with the lead, then precipitated by hydrogen sulfide (not ammonium sulfide). The precipitate is collected by filtering or centrifuging, washed slightly, dried, separated from the filter paper, placed in a crucible, carefully heated at first, and then ignited to volatilize the mercuric sulfide. The cooled residue is treated with 3 drops of buffer solution and mixed, and then 1 drop of 0.2 per cent freshly prepared solution of sodium rhodizonate is added. If lead is present, a red precipitate or coloration will appear. The identification limit is 5 micrograms lead in 10 ml.; the concentration limit is 1 to 2,000,000. It has been suggested that the lead might also be concentrated by electrolytic deposition. The microelectrode can be fumed in nitric acid and dried and the deposit then taken up in a drop of the buffer solution.

In the Presence of Other Materials. Table I shows that only thallium, silver, cadmium, barium, and stannous tin also react at pH = 2.8. However, if certain conditions are maintained, it is possible to detect lead with certainty, even though these interfering ions are present.

In the Presence of Insoluble Chlorides. Lead can easily be identified in the ordinary qualitative scheme if it is present along with silver chloride, mercurous chloride, and thallos chloride.

The chlorides thrown down by hydrochloric acid are not washed but are transferred directly to a crucible, dried by gentle warming, and then carefully heated to redness. Thallos and mercurous chloride are thus removed by volatilization. The cold residue is digested with 4 drops of strong ammonia water to dissolve silver chloride, and the contents of the crucible are then evaporated to dryness. Three drops of buffer solution and 1 drop of sodium rhodizonate are added. If the chloride precipitate contained lead, a red precipitate or coloration will appear. It is necessary to dissolve the silver chloride in ammonia because this salt melts and encloses lead chloride, which may thus be shielded from the sodium rhodizonate.

TABLE II. ALLOYS TESTED

Pb	Cu	Sn	Zn	Ni	Fe	Mn	Al	Result of Test
19.77	72.15	6.85	1.03	..	0.20	+++
2.41	60.52	0.13	36.54	..	0.28	..	0.12	+++
1.81	59.74	..	28.58	9.87	+++
1.08	85.73	12.28	0.97	1.34	+++
0.89	57.26	0.77	37.85	..	1.45	1.82	..	+++
0.56	85.34	11.87	0.74	1.48	+++
..	60.13	0.23	39.56	+++
..	89.17	9.54	..	1.44	---

This procedure, which can also be used to detect lead in the presence of all other metals, is far more sensitive than the usual method of dissolving the lead chloride in hot water and then adding a suitable reagent. The limiting proportion was determined in about 5 mg. of the mixed chlorides; the value is Pb:Ag = 1:5000.

In the Presence of Barium. The test solution is treated with concentrated sulfuric acid and then taken to definite fuming.

The mixed sulfates are brought onto a filter by means of alcohol and washed with this solvent until the sulfate test is no longer given. About 50 mg. of the washed precipitate are transferred to a spot plate, thoroughly mixed with 5 drops of a saturated solution of sodium acetate in 6 N acetic acid, and then dried by a current of heated air. One drop of water and 1 drop of sodium rhodizonate solution are then added. On stirring, the mass becomes violet if lead is present. If only minute quantities of lead are suspected, it is well to run a parallel test with pure barium sulfate. Limiting proportion, Pb:Ba = 1:10,000.

IN SOLID PRODUCTS. *In Ores and Minerals.* A small quantity (not more than 1 mg.) of the finely pulverized specimen is placed on a spot plate. Three drops of buffer solution are added and, after 2 minutes, 1 drop of sodium rhodizonate. A red precipitate or coloration signals the presence of lead.

The following minerals gave a positive reaction: galena (PbS), cerussite (PbCO₃), stolzite (PbWO₄), anglesite (PbSO₄), crocoite (PbCrO₄), and lead-bearing zinc blende (ZnS-PbS).

In Alloys. A few fragments of the alloy are rasped off by means of a fine file, the grease is removed with ether, and the alloy is treated on a spot plate with 3 drops of the buffer solution. The solid and liquid are kept in agitation for 2 minutes by blowing into the suspension through a pipet. A drop of sodium rhodizonate is then added, but is not stirred into the system. If the alloy contains lead, a red precipitate or coloration appears. A blank test employing 3 drops of the buffer solution and 1 drop of the reagent should be run when testing alloys that are very low in lead. The blank becomes completely colorless after a few minutes.

The relative lead content of a series of alloys can be judged by the intensity of the red coloration, provided that the parallel tests are run under like conditions, such as equal quantities and reaction times of the buffer and reagent solution.

Although stannous tin gives a positive reaction in the buffer solution, no significant quantities of this metal ion were derived from treatment of the alloys tested with the buffer solution. Other types of alloys may not yield the same noninterference, and consequently with such samples it may be well to apply the test with caution and reserve.

The alloys tested are listed in Table II.

If the lead content of the alloy is above 1 per cent, the specimen can be drawn several times across an unglazed porcelain plate, and the streaks tested with 1 drop each of the buffer and reagent. The red lead salt is clearly visible when formed by this simple procedure.

Metallic lead will obviously give positive results, by either of these procedures. If a lead bullet has passed through wood, for instance, the fact can be established by spot-testing the hole with rhodizonic acid.

In Pigments, Glass, etc. Several milligrams of the pulverized specimen are treated with 3 drops of the buffer solution and 1 drop of the reagent. The details of the procedure are the same as in testing for lead in alloys. Materials tested are given in Table III.

If oil colors or paints are being examined for lead, a small sample should be ashed and the residue carried through the procedure as outlined.

The foregoing studies demonstrate that sodium rhodizonate can be utilized for the speedy solution of certain analytical problems which are far more difficult and tedious when attacked by the earlier methods. Preliminary work in this laboratory indicates that sodium tetrahydroxyquinone (5) can be substituted for sodium rhodizonate in these new procedures. This is not surprising, since the two reagents have similar constitutions.

TABLE III. MATERIALS TESTED

Material	Formula or Lead Content	Result of Test
White lead	2PbCO ₃ ·Pb(OH) ₂	+++
Chrome red	2PbCrO ₄ ·Pb(OH) ₂	+++
Chrome yellow	PbCrO ₄	+++
Red lead	Pb ₃ O ₄	+++
Lead dioxide	PbO ₂	+++
Naples yellow	Lead antimonate	+++
Lead glass	About 30% Pb (as silicate)	++
Lead glass	About 0.3% Pb (as silicate)	+
Zinc oxide	About 0.9% Pb (as PbO)	+
Lead arsenate	PbHAsO ₄ (insecticide)	+++

Acknowledgment

The authors express their gratitude to Mario da Silva Pinto, director of the Laboratório Central da Produção Mineral, for his support in these studies.

Literature Cited

- (1) Chambers, M., *Chemist-Analyst*, **27**, 8 (1938).
- (2) Feigl, F., *Mikrochemie*, **2**, 188 (1924); *Z. angew. Chem.*, **39**, 393 (1936).
- (3) Feigl, F., "Qualitative Analysis by Spot Tests", 2nd ed., pp. 137, 138, 204, New York, Nordemann Publishing Co., 1939.
- (4) Grant, J., *Ind. Chemistry*, **8**, 169, 217 (1932).
- (5) Gutzeit, G., *Helv. Chim. Acta*, **12**, 713, 829 (1929).
- (6) Kolthoff, I. M., *Pharm. Weekblad*, **62**, 1017 (1925).
- (7) Kolthoff, I. M., "Acid-Base Indicators", p. 266, New York, Macmillan Co., 1939.
- (8) Mutschin, A., and Pollak, R., *Z. anal. Chem.*, **106**, 385 (1936); **107**, 18 (1936); **108**, 8, 309 (1937).
- (9) Streibinger, R., and Zombory, L. v., *Ibid.*, **79**, 1 (1929); **105**, 346 (1936).
- (10) Zombory, L. v., *Ibid.*, **110**, 278 (1937).