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Toluene-3,4-Dithiol and Its Derivatives as Analytical Reagents

A new approach to qualitative inorganic analysis

Nineteenth century chemists employed a limited number of simple analytical techniques such as the flame-, borax bead, and charcoal-block tests. In 1905, Tschugaev discovered that dimethylglyoxime gave a red precipitate which was uniquely characteristic for the nickel ion. This was the first widely used organic spot-test reagent for a metal and, since that time, organic compounds have been used in inorganic analysis in bewildering profusion. This abundance of reagents has led to much confusion in the minds of beginning students. Thus they ask what determines which particular reagent should be used when confirming, say, bismuth or tin? Why? Exactly what chemical principles are involved? How do they operate? These and similar questions confound the beginner (and not infrequently the research chemist!) who concludes that inorganic analysis employing organic reagents is more an art than a science!

The purpose of this article is to show that these difficulties are readily overcome when analysis is thought of as a *unity*. The traditional basis of analysis is perfectly rational. Cations are divided into groups depending upon precipitation by hydrochloric acid, hydrogen sulfide in acid solution, ammonia in presence of ammonium salts, hydrogen sulfide in alkaline solution and ammonium carbonate. What is required is to relate the confirmations of each element to the basic scheme.

If we agree that organic reagents are desirable in inorganic analysis, a logical approach is to look for organic analogues of the Group precipitants, so that the thiophilic elements (those precipitated as insoluble sulfides) may be separated from those which are oxyphilic (those precipitated as insoluble hydrated oxides). Thus, a search is first made for organic analogues of hydrogen sulfide, which will precipitate the thiophilic elements. Secondly, a search is made for organic analogues of ammonium hydroxide, considered as a derivative of water, which will precipitate the oxyphilic elements.

Taking hydrogen sulfide first, the organic compound we look for will be:

(1) An aromatic compound since resonance in the ring will aid in the development of brilliant color. Further, aromatic compounds are only sparingly soluble in water.

(2) A compound with two —SH groups since, in H_2S, there are two acidic hydrogen atoms bonded to sulfur. As in the case of H_2S, aromatic SH-containing compounds are weak acids, the dissociations of which are dependent upon the *p*H of the solution.

(3) An aromatic compound containing two —SH groups in the ortho position, since these readily form stable, usually water-insoluble, chelates with metal cations.

Bearing the above points in mind the reagent of choice is seen to be benzene-1,2-dithiol. Unfortunately, this compound is difficult and expensive to make. Toluene-3,4-dithiol ("dithiol," DT), is readily available, not too expensive, and is extremely similar to hydrogen sulfide in its properties. Dithiol gives highly selective reactions for most of the metals which are precipitated by hydrogen sulfide. When dithiol fails, the structurally-similar, readily available, and more strongly acidic quinoxaline-2,3-dithiol (QDT) is employed. This is a valuable reagent for nickel and is superior to dimethylglyoxime.[4,5]

Table 1

Group	Element	Reagent used for confirmation	Concentrations necessary for good reactions (parts per million)
I	Ag	DT	5
	Hg	DT	50
	Pb	DT	5
IIA	Hg, Pb	As above	...
	Bi	DT	1
	Cu	DT	1
	Cd	H_2S	50
IIB	As	DT	1
	Sb	DT	50
	Sn	DT	1
III	Fe (Also precipitates in Group 4)	Catechol or DT	1, 1
	Cr	Catechol	50
	Al	Alizarin	...
IV	Co	DT	1
	Ni	QDT	1
	Mn	DT	1
	Zn	H_2S or DT	50, 50

Exactly similar logic leads to the choice of benzene-1,2-diol ("catechol") as the organic analogue of ammonium hydroxide. Two of the Group III metals (Cr and Fe) give characteristic reactions with catechol, but for aluminum the functionally similar alizarin is employed. Certain of the rarer Group III elements react with tannic acid or tannin, which is a catechol-like compound of higher molecular weight.

Remembering that Group I elements, which are usually precipitated as chlorides, are also precipitated as sulfides in acid solution it is not surprising that dithiol can be used to confirm them. Thus, confirmatory tests for the sixteen common elements in Groups I to IV become quite logical (Table 1).

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[1] For reprints: 783 Cereza Drive, Palo Alto, Calif. This article appeared in a different form in *School Science Review*, **40**, No. 140, pp. 41–51 (1958).

Dithiol and Its Use

Since this article is about dithiol, which may be unfamilar to some readers, we shall now describe its properties and the ways in which it is used. Dithiol is a colorless solid (mp 35°) possessing a characteristic, faint, but not unpleasant odor. Like hydrogen sulfide it is a mild reducing agent, though barely so in strong acid, and it is oxidized by atmospheric oxygen to the polymeric disulfide, $(C_7H_6S_2)_n$. When first precipitated this polymer resembles sulfur in appearance and, like sulfur, is soluble in carbon disulfide, but few other solvents.

Dithiol precipitates the same metals as does hydrogen sulfide and usually under similar conditions. Its derivatives, which in this article we shall refer to as *mercaptides*, are sometimes (as with Sn) less soluble than the sulfides, and sometimes (as with Pb) more soluble. Many sulfides (e.g., CuS and CoS) dissolve readily in an alkaline solution of dithiol. The mercaptides of Group IIB metals dissolve in alkali, whereas those of Group IIA are insoluble, although they may dissolve in an alkaline solution of dithiol. This latter phenomenon may be compared with that of the solubility of mercuric sulfide in alkaline sulfides.

The resemblance between hydrogen sulfide and dithiol extends to many other reactions. For example, both reagents give a positive nitroprusside reaction. Cobalt and nickel mercaptides, like the corresponding sulfides, fail to precipitate except in weak acid but, once precipitated, they are not dissolved except by a much stronger acid. Among the common cations arsenic is unique in the ease with which it gives colloidal solutions of arsenic mercaptide or sulfide. Without doubt, dithiol could replace hydrogen sulfide entirely in analysis, but the higher cost is discouraging. For confirmatory tests, however, only traces of dithiol are required so that the cost is very low.

Dithiol complexes with metals are remarkable in that all the colors of the spectrum are represented, with almost no two colors identical. Even when colors are similar they are often formed under entirely different conditions (see Table 2) or have a totally dissimilar appearance (e.g., Bi and Sn). Moreover, the reactions are highly sensitive and compare very favorably with established procedures. Frequently, the reactions are greatly superior, as in the cases of tin, cobalt, tungsten, and molybdenum.

Dithiol has a remarkable and analytically useful property not shared by hydrogen sulfide. To illustrate, let us imagine that hydrogen sulfide is passed into a hot weakly acid solution of copper and cadmium ions. Black cupric sulfide precipitates first, then quite suddenly the newly-formed precipitate becomes yellow as cadmium sulfide forms. Thus, a sharp change in color makes it possible to separate the two metals.

Such separations are rarely possible, however, because sulfides coagulate poorly and their colors show so little variation. Moreover, the colors of certain sulfides vary considerably with time immediately after they have been formed. With dithiol these difficulties do not arise for, added to a mixture of cations in solution, good separations usually result. Even in solutions containing many cations the color of the freshly-formed precipitate shows which element is being precipitated. It is often helpful to add a few drops of dense solvent (e.g., ethylene dichloride) to remove the precipitates as they are formed from the warm solution. In this way a change in color of the freshly-formed precipitate may be rendered at once more obvious. For example, by mixing 0.01 *M* solutions of cations, two at a time, and adding dithiol, the student can arrange the complexes in the order of their solubility products and at the same time he becomes familiar with their colors.

The mercaptide complexes usually precipitate with extraordinary ease, probably due to the presence of the hydrophobic aromatic ring. As the mercaptides are very insoluble dithiol can replace hydrogen sulfide on the surface of sulfide precipitates. Thus, if a colloidal solution or suspension of sulfides stubbornly refuses to precipitate, it may be boiled with a trace of dithiol. The colloidal sulfide particles become less easily wetted by water (i.e., become hydrophobic), coagulate rapidly, and precipitate. It follows, therefore, that in acid solution the value of hydrogen sulfide as a reagent for precipitating thiophilic cations is greatly enhanced by the addition of a trace of dithiol.

Diacetyldithiol (DADT) is an even better catalyst for improving precipitation by hydrogen sulfide. In acid solution this compound is stable and, unlike dithiol, is not volatile with steam. In dilute mineral acids, diacetyldithiol causes arsenates and molybdates to decompose smoothly within a few minutes, none of the usual difficulties being encountered. With the more common elements the precipitates obtained are the usual sulfides, since only a trace of the organic compound is added.

Table 2. Colors of Dithiol–Cation Precipitates

Formed in	Colorless	Brown	Black	Red	Orange	Yellow	Green	Blue	Purple or violet
10 *N* HCl	—	—	—	Pd Au (brown-red)	—	Te Se Rh (brown-yellow)	Re	W	Te (excess DT)
6–10 *N* HCl	Ge	Ru	Ir	—	—	Hg As(very pale)	—	—	Os
1–6 *N* HCl	—	—	Cu Co	Bi Sn(II)	Sb(III)	Ag	W Mo	—	Pt
1 *N* HCl or acetic acid	Cd Zn Ga In	—	Co Fe Ni	—	Tl	Pb Sn(IV)	—	—	—
Alkali including pyridine (Py)	Most cations	Mn	—	Fe(II) Sb(V)	Cu(NaOH) Tl	—	Ru(III) Cu(Py) Ni V	Co	—

Diacetyldithiol also coagulates the colloidal solution of sulfur obtained by acidifying a solution of thiosulfate.

In Group IV it is customary to dissolve the nickel and/or cobalt sulfide precipitate in aqua regia, or similar solvent, before testing for nickel and cobalt, respectively. This is unnecessary, however, because the precipitates immediately dissolve in a suitable DT or QDT solution to give colors characteristic of the two metals.

Like hydrogen sulfide, dithiol is difficult to keep in the free state. In solution the disulfide precipitates, just as in a solution of hydrogen sulfide free sulfur is precipitated. Dithiol is most conveniently stored as the colorless zinc complex (ZDT), $C_7H_6S_2Zn$, which can be kept indefinitely. It is usually sufficient to add this *directly* to the solution to be analyzed. The reactions of DT are immediately obtained on warming. In very rare instances zinc must be absent, and when this is so ZDT is added to hot dilute acid and the DT is extracted with chloroform or ethylene dichloride. Alternatively, a solution of DT can be obtained within a few seconds by warming DADT with pyridine or alcholic KOH.

It is hoped that this brief summary of the uses of dithiol and catechol-like reagents may point the way to a more rational approach to inorganic analysis. Although DT is somewhat more expensive, on a weight basis, than many other reagents, the quantities required are small. For example, a class of 15 students, which employed ZDT for confirmatory tests only, used less than 0.5 g in 30 hours of practical analytical work. Savings in servicing, by making one or two reagents do what many did before, are also considerable. Again, the time of the student (or research worker) is frequently wasted in looking for reagents so that a reduction in their number is to be welcomed.

Paradoxically enough, the older chemists were probably correct in believing that qualitative inorganic analysis requires but few reagents. Perhaps the modern trend to discover one reagent specific for each cation is a retrogression!

The reagents and experimental procedures employed in the qualitative analysis of cations are given in the following section. Readers requiring further information are referred to the recent papers by Clark.[2] The use of ZDT as a reagent for ketose sugars is described by Clark and Neville.[3]

Reagents

Zinc Dithiol (*ZDT*) is a stable white powder affording a convenient source of dithiol (DT). It may be used dry or 0.5–1.0 g may be rubbed with alcohol and made up to give a suspension in 100 ml of 95% alcohol. The bottle is labeled "shake before use" and is provided with a teat-dropper. Between 1–4 drops suffice for most tests.

Procedures

(1) Add ZDT directly to the solution to be tested. Only rarely (as in testing for Zn and Mn) does the zinc interfere.

(2) Add ZDT to alcohol. Add a few drops of conc. HCl. A colorless clear (or nearly clear) solution of DT is obtained. The solution should be used within 2–3 hours.

(3) If DT free from Zn is required, shake dry ZDT with dil. HCl and heat until oily drops of DT appear. Add a dense solvent (chloroform or ethylene dichloride) and cool. Remove portions of the lower layer, which is a Zn-free solution of DT, with the aid of a dropper as required. If the lower layer is not clear, insert a plug of cotton before using the dropper.

Diacetyldithiol (*DADT*) is a white crystalline solid, mp 48°, soluble in all organic solvents. Should be stored in a dark bottle. A metal spatula should not be used in handling, as discoloration may result.

Procedures

(1) To prepare a coagulant for sulfides and sulfur, dissolve approximately 1 mg in 0.5 ml of alcohol. Use one drop. The solution is not stable beyond a few weeks.

(2) Melt one pellet of KOH (0.1 g) with one drop of water. Add 1 ml of alcohol and a few crystals of diacetyldithiol. Heat and hold at the boiling point for 10–15 seconds. The solution now contains DT free from Zn.

(3) Add a few crystals to 1 ml of pyridine. After warming, this mixture gives the reactions of free DT.

Quinoxaline-2,3-Dithiol (*QDT*) is a dark yellow stable powder, mp 345°, with decomposition.

Procedure

Dissolve 0.1 g in 50 ml 2*N* NaOH and add 1–2 g of sodium sulfide crystals. The solution is stable for 1–2 months, after which it reacts slowly and, eventually, hardly at all. Used as a test for Ni.

Uses of Reagents in Elementary Analysis

For the most part the tests are highly sensitive, and it is usually sufficient to employ one drop of the diluted test solution. Methods may be used on the traditional scale or, with obvious modifications (e.g., for "filter," read "centrifuge," etc.), for semimicro work. Owing to the violent gas evolution, however, the suggested separation for Group IIB is less suitable for the latter.

Preliminary Tests. As the consumption of ZDT is likely to be greater if the solid is used, these tests may be omitted with elementary students if desired.

I. To a drop of the test solution add excess conc. HCl:
(1) Add solid ZDT in excess and warm.
(2) Then add slowly 3–4 vols. of water, noting any colored precipitates formed. Boil.
(3) Finally, add sodium acetate crystals in excess.

(1) White milky suspension in strong acid probably indicates As. Oxidizing agents act similarly. If the test is repeated with the addition of a reducing agent, e.g., crystals of $SnCl_2$, the reaction is highly selective. Some rarer elements give colored precipitates which coagulate rapidly and do not usually interfere.

(2) Very pale yellow ppt. Characteristic appearance:

Climbs wall of tube	Hg
Yellow precipitate	Ag
Black or gray precipitate	Cu
Orange precipitate (oily on boiling)	Sb
Magenta-red precipitate	Sn
Brick-red precipitate	Bi

Since the precipitates form at different acidities and coagulate rapidly, it is frequently possible to identify the presence of more than one metal. However, owing to the oily nature of the product that it gives, Sb tends to mask other reactions.

(3)	Bright yellow precipitate	Pb
	Black or dark precipitate	Fe, Co, Ni

(With Fe, Co, Ni, excess DT colors the liquid. See below.)

II. To a drop of the test solution add a few drops of pyridine and 0.1–0.5 mg of ZDT (or a few crystals of DADT). Warm:

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[2] Clark, R. E. D., *Analyst*, **82**, 177, 182, 760 (1957); **83**, 103, 396, 431 (1958); **84**, 16 (1959).

[3] Clark, R. E. D., and Neville, R. G., *J. Org. Chem.*, **24**, 110 (1959).

Green color	Cu (Possible confusion with Ni)
Blue color	Co
Magenta-red color (intense with DADT)	Fe

The original substance with NaOH and excess ZDT gives an *orange* color if Cu is present.

Precipitation of Group 2 Metals by Hydrogen Sulfide. Adjust the acidity of the solution to 0.3–0.4 *N* in the usual manner. Add one drop of DADT in alcohol (see above). Pass H_2S as usual. Finally add a further drop of reagent and boil off the alcohol. Proceed as usual.

Confirmatory Tests for Cations

Group I. Separate as usual.

Hg. Dissolve black residue on filter in HCl + Br_2-water (a trace of potassium chlorate may always be used in place of Br_2-water). Boil off Br_2 and dilute. Add ZDT. Pale yellow precipitate tending to creep up walls of tube indicates *Hg.*

Ag. To a few drops of ammoniacal solution add large excess conc. HCl and warm until first formed precipitate redissolves. Add ZDT. Add drops of water slowly. Yellow ppt. forming suddenly indicates *Ag.*

Pb. To solution containing $PbCl_2$ in *hot* water add ZDT. Brilliant yellow ppt. indicates *Pb.*

Group II. Precipitate Group II metals as above using H_2S and DADT. Separate Group IIA from Group IIB as usual, using 0.5–2.0 *N* KOH or 1% LiOH.

Group IIA. Separate in the usual way. (Good separation can be effected by means of DT but the method is likely to prove expensive for elementary classes.)

Hg. Dissolve and test as in Group I.

Pb. Precipitate consists of $PbSO_4$. Dissolve a few mg of ZDT in dil. NaOH and pour solution through the filter. The $PbSO_4$ is immediately stained a brilliant yellow. Incomplete removal of Pb from the solution by means of sulfuric acid does not interfere with subsequent tests.

Bi. Pour hot dil. HCl through the filter to dissolve ppt. of $Bi(OH)_3$. To portion of filtrate add ZDT and boil. Chill quickly. Brick-red ppt., partly or wholly soluble on boiling, indicates *Bi.*

Cu. To 1–3 drops of ammoniacal solution add excess ZDT. Intense orange color indicates *Cu.* (If ZDT is not in excess a dark ppt. forms.)

Cd. To second portion of ammoniacal solution add excess $Na_2S_2O_4$ and boil. Filter from Cu. Pass H_2S. Yellow ppt. indicates *Cd.*

Group IIB.

To the alkaline extract from Group 2A add an equal vol. of conc. HCl. Heat to boiling. Filter from As_2S_3. To the filtrate add half its vol. of ethylene dichloride followed by Zn dust until the violent reaction moderates. Sb as metal collects in the lower solvent layer and $SnCl_2$ remains in the dilute acid. (If the acidity has been lowered too much by the Zn, Sn may precipitate as metal together with Sb. It is readily dissolved by the addition of more acid in which Sb is insoluble.) Use dropper to separate layers.

As. Dissolve ppt. in conc. HCl + Br_2-water. To 1 drop add conc. HCl in excess plus crystals of pure $SnCl_2$ or NaH_2PO_2. Add ZDT and warm. Immediate white emulsion (turning red with much As present) indicates *As.*

Sb. To the suspension of metal in ethylene dichloride add conc. HCl and Br_2-water and heat. Boil off Br_2 and solvent. Add ZDT and dilute somewhat. Heat. Orange ppt. melting to orange drops on surface indicates *Sb.* (*Note:* Sb(V) gives a magenta-red color with Zn-free DT and pyridine. This reaction is much more sensitive than the above, but confusion with the similar color given by Fe is possible.)

Sn. To aqueous layer containing $SnCl_2$ add ZDT and warm. Magenta-red ppt. indicates *Sn.*

Group III. Separate as usual.

Fe. Transfer a trace of the ppt. of $Fe(OH)_3$ on the end of a glass rod to a few drops of pyridine containing either (*a*) a few crystals of catechol, or (*b*) a trace of DADT or Zn-free DT. (If ZDT is used the color is much less intense.) Warm. An intense blue or red color, respectively, indicates Fe.

Cr. Acidify a portion of the solution containing chromate with dil. H_2SO_4. Boil to destroy H_2O_2. Cool. Add a few mg of catechol. Solution darkens, finally becoming black if Cr is present. (The test has proved more reliable and more sensitive than the usual peroxide test, but fails if hydrogen peroxide has not been mostly destroyed.)

Al. Test with alizarin or other catechol-like reagent as usual.

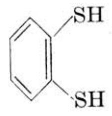
Group IV. Separate as usual. After extracting with dil. HCl, test a portion of the black ppt. for Co and Ni directly.

Co. Transfer a trace of the ppt. on the end of a glass rod to a few drops of pyridine containing ZDT. Warm gently. Sky-blue color indicates *Co.* (Excess of Co or too little ZDT may give rise to a greenish color which is equally definite.)

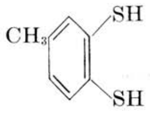
Ni. Transfer a trace of the ppt. to a few drops of QDT reagent (see above). Warm. A red or orange color indicates *Ni.*

Mn. Dissolve ppt. of MnO_2 in HCl by boiling. Add sodium acetate crystals in excess and Zn-free DT. Intense greenish brown color indicates *Mn.*

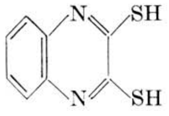
Zn. Present as sodium zincate in alkaline filtrate. Acidify with acetic acid. Add Zn-free DT in ethylene dichloride and shake. In presence of Zn a bulky white ppt. forms in the droplets of solvent which may appear to solidify.



Benzene 1,2-dithiol



Toluene-3,4-dithiol (DT)



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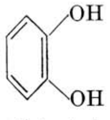
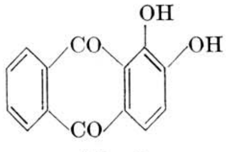


Catechol



Alizarin

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[4] Morrison, D. C., and Furst, A., *J. Org. Chem*, **21**, 470 (1956).

[5] Skoog, D. A., Lai, Ming-Gon, and Furst, A., *Anal. Chem.* **30**, 365 (1958)