

# MUTUAL INTERFERENCE IN THE MICROCHEMICAL DETERMINATION OF ORE MINERALS

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## INTRODUCTION

The use of microchemical methods is spreading rapidly, both for the qualitative and quantitative determination of elements. Microchemistry offers a decided advantage over "bulk" methods, not only because of the greater speed with which the determinations can be carried out, but also because of the very small amounts of material required for a test. Microchemical methods are particularly valuable in determining the composition of the small inclusions in ores and metallurgical products.

Most of the reagents used are sufficiently sensitive to show the presence of 0.005 per cent or less of the desired element. Needless to say, if such minute quantities of an element are to be identified, it is essential that the procedure of the test be carefully followed and the utmost caution taken that there is no pollution of the reagent or the test drop. Despite such care, it frequently happens that the test obtained is not wholly satisfactory. Either the color of the precipitate is unusual, the form is changed or entirely different, or sometimes no test is obtained when previous observations have indicated that the element should be present. When such changes occur—and they occur frequently, even in the hands of skilled technicians—the observer is never certain whether they are due to variations in the  $p_H$  of the solution, concentration of reagent or solution, or to the presence of some interfering anion or cation. The first two variables can be controlled by proper attention to the procedure of the test; in many cases the last variable—presence of an interfering anion or cation—is beyond control. Often, much time could be saved by recognizing that a given variation in the precipitate is caused by the presence of another element. In fact, some of the interferences are as characteristic of the interfering element as any other known test.

The presence of a variety of elements in the test drop is due either to a poor sample or to a complex mineral. A poor sample is obtained if the original area of the mineral or inclusion is too small. In this case, allowance can usually be made for the presence in the solution of elements of the host mineral, although their presence may cause notable interferences. Where the mineral varies in composition there may be no hint of the presence of elements, other than those expected in the mineral, until trouble is encountered in the testing.

The sulphide minerals are notoriously impure; in fact, the use of microchemistry has been responsible in considerable part for the recognition of the extent of isomorphic replacement. Sometimes the presence of these "impurities" is unimportant and can safely be ignored, particularly among the more complex sulphide salts. Many times microchemistry is employed, not to determine the major constituents, but to determine the presence of small amounts of other elements replacing the major constituents in the mineral. Consequently it is essential to have sensitive tests and also to know the limitations of these tests.

It might be possible to devise two tests for every element. One test would be sensitive only to large amounts of the element, and would serve to indicate those elements present in amounts sufficient to enter into the formula of the mineral. The other test might be very sensitive and serve to show small amounts of the element present as "impurities." Such a system, however, would involve the use of many more reagents, more time in testing, and would inevitably fail in border line cases. Moreover, the same results can be obtained by controlling the concentration of the test drop, and using a sensitive precipitant.

Very little attention has been given in the literature of microchemistry to the effect of the presence of other elements on the nature of the precipitate for any particular test. Some reference to the interference of particular elements on some tests are to be found scattered through the publications of Short,<sup>1</sup> and of Chamot and Mason,<sup>2</sup> but the list is far from complete. It is the purpose of this paper to collect and check all interferences that have been previously described and in addition to describe hitherto undescribed interferences in the standard microchemical tests for the twenty most common elements of the metallic minerals. Suggestions are made for circumventing some of the difficulties occasioned by these interferences.

Not all of these twenty elements can interfere in each of the tests studied. Some of them are stable only in nitric acid, some only in hydrochloric acid, and others are stable in both acids. Likewise the reagents investigated require either a nitric, hydrochloric, neutral, or alkaline solution to produce satisfactory precipitation. All of the twenty elements stable in that solution are considered as potential interfering elements. No elements are excluded from investigation because they are not known to occur together in a mineral. As far as the authors are aware, no mineral containing gold and cadmium is known at present, but that does not

<sup>1</sup> Short, M. N., *Microscopic Determination of the Ore Minerals: U. S. Geol. Survey, Bull.* **825**, 1931.

<sup>2</sup> Chamot, E. M., and Mason, C. W., *Handbook of Chemical Microscopy*, Vol. II: Wiley and Sons, New York, 1931.

mean that one may not be found in the future, or that gold may not occur in such minute disseminations in a cadmium mineral as to be inseparable by mechanical means. Moreover, it is hoped that the results of this study may be of value in fields other than mineralogy, in which event there might be no limitation to the association of the elements.

The present scheme for the systematic testing of a mineral by microchemical methods—as outlined in *U. S. Geol. Survey, Bull.* 825—has been in use for several years and gives satisfactory results for most ore minerals. The purpose of the present work is to increase the usefulness of that scheme by pointing out some of the pitfalls for the unwary and by clarifying interpretation of the results under particular circumstances. Under certain conditions, mentioned later, the tests recommended in that procedure are misleading or entirely unsatisfactory. Resort may then be made to other tests or to a different procedure. This study brings out the need for alternate tests for some of the elements which seriously interfere and commonly occur together.

The authors are indebted to Professor M. N. Short, of the University of Arizona, for the use of his lists of the reactions of individual elements with several of the reagents. Descriptions of some of these reactions have been modified by the authors, who performed the tests under somewhat different conditions. Professor A. O. Beckman of the California Institute has given the authors much valuable advice concerning possible chemical explanations of some of the interference reactions noted. Mr. M. H. Evans, California Institute, discovered and studied the thiourea test for selenium, and the authors acknowledge his kindness in permitting its inclusion in this paper.

#### PROCEDURE

For each of the twenty elements studied a solution containing 1 per cent of the metallic ion (not of the salt from which the ion was derived) was prepared in either 1 per cent  $\text{HNO}_3$  or 1:5  $\text{HCl}$  as indicated below, except the nitric solutions of tellurium, selenium and bismuth. The standard solution of tellurium was 0.1 per cent in 10 per cent nitric acid, of selenium was 1 per cent in 5 per cent nitric, and of bismuth was 1 per cent in 10 per cent nitric. The use of the elements in acids of the aforementioned concentrations closely simulates the actual conditions under which the tests give the most satisfactory results. A part of these standard solutions was then diluted to give a 0.1 per cent or a 0.01 per cent solution of the element. Each element for which the test can be used was tried in the presence of as many of the remaining twenty ions listed below as were stable under the conditions of the test.

TABLE 1. ELEMENTS INVESTIGATED

Element stable in 1 per cent HNO <sub>3</sub>	Element stable in 17 per cent HCl	Element stable in both 1 per cent HNO <sub>3</sub> and 17 per cent HCl	
Cd ++	Sb +++	As +++	Hg ++
Pb ++	Au +++	Bi +++	Ni ++
Ag +	Sn ++++	Co ++	Se
Te	Ti +++	Cu ++	Zn ++
		Cr +++	Cl -
		Fe +++	NO <sub>3</sub> -
		Mn ++	SO <sub>4</sub> --

Two distinct conditions were recognized in making the tests: first, where only one of the cations (positive metallic ions) gave a useful test with the particular reagent (thus, the thiocyanate test for iron in the presence of manganese); secondly, where both cations gave a useful test with the particular reagent (thus, the thiocyanate test for iron in the presence of copper).

When only one of the cations gave a useful test, a 0.1 per cent solution of the reacting cation was first tested in the presence of a 1 per cent solution of the other ion. If no reaction was obtained, a 1 per cent solution of the reacting cation was tested in the presence of a 1 per cent solution of the other ion. If still no reaction was obtained, a 1 per cent solution of the reacting cation was tested in the presence of a 0.1 per cent solution of the interfering ion. This method gives a range of concentration of 100 per cent. In some tests, the solution strengths were 1, 0.1 and 0.01 per cent. Different concentrations of anions were used. These concentrations will be mentioned later.

Where both metals gave a useful reaction with the particular reagent, a 0.1 per cent solution of the first ion was run in the presence of a 1 per cent solution of the second ion. Then a 0.1 per cent solution of the second ion was run in the presence of a 1 per cent solution of the first ion. Where either or both of these groupings did not give the desired reactions for both elements, the reaction was run with both metals present in a 1 per cent solution.

In the interference reactions described throughout the paper, *the list* gives only the *lowest relative proportion of the interfering element* which will cause interference, except in special instances specifically mentioned. Thus, when a 1 per cent cobalt solution is described as interfering with a 1 per cent cadmium solution in the thiocyanate test, it is to be assumed, unless otherwise stated, that a 1 per cent cobalt solution will likewise interfere with a 0.1 per cent cadmium solution, but that a 0.1 per cent cobalt solution will not interfere with a 1 per cent cadmium solution.

Each reaction was watched throughout the period of evaporation until the reagent began to precipitate out from the drop. In a climate where the humidity is not extremely low, this procedure often entails a relatively large expenditure of time, but, in the presence of other ions, many of the most useful reactions are much delayed. All extraordinary delays in the reactions are noted in the article, but to consider all delays in the reactions as interferences (within the definition to be given) would be to increase very greatly the already large number of interferences noted. It is, therefore, regarded as advisable to watch the drop throughout the period of evaporation.

"Interference" is used throughout to mean any marked change in size, shape, or color of the precipitate, as well as the rapidity of precipitation. If the precipitate of the interfering element is so bulky or similar to that of the reacting element as to impede the recognition of the test, it would also be classed as an interference. Of course, the size, shape and rapidity of precipitation vary with the relative concentration of the test drop and reagent and consequently comparisons were only made between tests containing the same quantity of the reacting cation. Changes in the color, size or shape of the precipitate which were not great enough to seriously affect the recognition of the test were not considered as interferences. Throughout the work, the tendency was to regard all tests as satisfactory unless there was serious doubt as to the identity of the precipitate.

A "major interference" is one in which the proportion of the interfering ion is equal to or less than the reacting ion. In a "minor interference," the interfering ion is ten times or more abundant than the reacting ion.

For each test studied in detail, the information is presented as follows:

- (a) The reaction of each element with the particular reagent.
- (b) Where the test is useful for more than one element a chart is given showing the interference phenomena for each element in the presence of each of the possible interfering ions.
- (c) A description of each of the interference reactions.
- (d) A discussion of the particular test with regard to its value for detecting each metal for which it can be used, together with possible methods for remedying some of the interferences noted.

The tests are taken up in the following order:

- |                                   |                         |
|-----------------------------------|-------------------------|
| 1. Ammonium molybdate             | 6. Potassium iodide     |
| 2. Potassium mercuric thiocyanate | 7. Double iodide        |
| 3. Dimethylglyoxime               | 8. Thiourea             |
| 4. Ammonium bichromate            | 9. Sodium bismuthinate. |
| 5. Cesium chloride                |                         |

### Symbols

For the sake of brevity a few symbols are used throughout the paper and are here listed:

- (C, pp.—) Interference discussed in whole or in part in Chamot and Mason.<sup>3</sup>  
 (S, pp.—) Interference discussed in whole or in part in *Bulletin* 825.  
 (W, pp.—) Spot reaction described by Watson.<sup>4</sup>  
 O No mutual interference.  
 X Mutual interference—described in text of article.  
 — Can not be present in solution together.  
 + Not possible to determine the extent to which the cation interferes with the reaction since it is in solution with an interfering anion.  
 (1) Concentration in per cent of the element in solution. Thus (1) denotes 1 per cent of the element, (0.1) denotes 0.1 per cent.

## 1. AMMONIUM MOLYBDATE TEST

### *Individual Reactions*

A drop of the element in 1 per cent nitric acid solution is allowed to partly evaporate and then a drop of the reagent added and the evaporation slowly completed on a warm hot plate. The residue is dissolved in 1:7 HNO<sub>3</sub>.

- Ag No precipitate.  
 As Lemon yellow octahedra.  
 Bi No precipitate.  
 Cd No precipitate.  
 Co No precipitate.  
 Cu No precipitate.  
 Cr No precipitate.  
 Fe No precipitate.  
 Hg On addition of ammonium molybdate a precipitate of small black grains slowly forms. After evaporation and addition of nitric acid, there remains a peripheral deposit of small black cubes, white or faintly yellow in reflected light.  
 Mn No precipitate.  
 Ni No precipitate.  
 Pb On addition of ammonium molybdate a slow precipitation of small black grains occurs. After evaporation and addition of nitric acid, there remains a heavy precipitate of black cubes and grains around edge of drop. These are white in reflected light.

<sup>3</sup> Chamot, E. M., and Mason, C. W., *op. cit.*

<sup>4</sup> Watson, J. Adam, Colour reactions in the micro-chemical determination of minerals: *Mineral. Mag.*, vol. 24, pp. 21-34, 1935.

- Se Selenium does not redissolve in nitric acid but remains as a brownish, fine-grained precipitate, white in reflected light.
- Te Tellurium does not redissolve in nitric acid but remains as a fine-grained precipitate of black grains, white in reflected light.
- Zn No precipitate.

#### *Interference Reactions*

No interference was noted in the test on a (0.01) arsenic solution in the presence of a (0.1) solution of Ag, Bi, Cd, Co, Cu, Cr, Fe, Mn, Ni, Se, Te, and Zn.

A (1) solution of Hg or Pb does not interfere with the test on a (0.01) As solution except that the Hg and Pb precipitates tend to mask the As test. The color of both the Ag and Pb precipitates is white.

The presence of much HCl or H<sub>2</sub>SO<sub>4</sub> in the test drop appears to decompose the ammonium molybdate and ruin the test.

## 2. POTASSIUM MERCURIC THIOCYANATE TEST

### *Individual Reactions*

A drop of a (3) solution of the reagent is merged with a drop of the element in (1) HNO<sub>3</sub> where possible, otherwise in the solution previously mentioned. All reactions occur in a (0.1) solution of the element unless otherwise stated.

- Sb No precipitate.
- As Gray, peripheral, amorphous precipitate. Good colorless, hexagonal plates are formed in a (1) solution. Precipitate very slow in forming.
- Bi No precipitate.
- Cd Blunt, white prisms which usually have cavities at each end. Reaction delayed in a (0.1) solution.
- Co Blue prisms and spherules.
- Cu Greenish-yellow, moss-like aggregates and prisms.
- Cr No precipitate.
- Au Yellowish-brown, moss-like aggregates, gold colored in reflected light. Not present in (0.1), but present in a (0.3) solution.
- Fe Solution turns red. Rather faint in (0.1).
- Pb White granular amorphous precipitate.
- Mn No precipitate.
- Hg Mercuric ions give no precipitate.
- Ni White to brown spherules. Test delayed in (0.1).
- Se Numerous, peripheral, greenish-yellow globules, very late forming. As drop dries up, elemental selenium is deposited.
- Ag Curdy, white, fine-grained precipitate.
- Te No precipitate.
- Sn No precipitate.
- Ti No precipitate.
- Zn White, feathery crosses.

## Interference Chart

Element Tested for	Interfering Elements																				
	Sb	As	Bi	Cd	Co	Cu	Cr	Au	Fe	Pb	Mn	Hg	Ni	Se	Ag	Te	Sn	Ti	Zn	Cl	SO <sub>4</sub>
Cd	+	○	○		×	×	○	+	×	○	○	○	×	○	×	○	+	+	×	×	×
Co	○	○	○	○		×	○	×	×	○	○	○	×	○	○	○	○	○	×	○	○
Cu	○	○	○	○	×		○	×	×	○	○	○	×	○	×	○	×	×	×	○	○
Au	○	○	○	○	×	○		○	○	○	○	○	○	○	○	○	○	○	○	○	○
Fe	○	○	○	○	○	○	○		○	○	○	○	○	○	×	○	○	○	○	○	○
Ni	+	○	○	×	×	×	○	+	○	○	○	○		○	○	○	+	+	○	×	○
Ag	-	○	○	○	○	×	○	-	○	○	○	○	○	○		○	-	-	○	×	○
Zn	+	○	×	×	×	×	○	+	○	○	×	×	×	○	○	○	○	○		×	○

## Interference Reactions

## Cadmium

Cd (1) Sb (0.1)	No Cd test. Performed in 1:5 HCl.
Cd (1) Co (1)	All crystals colored blue. Cd not easily recognizable.
Cd (0.1) Cu (1)	Poor Cd test.
Cd (1) Cu (1)	Fair Cd test. Many crystals are tapered and colored light green.
Cd (1) Au (1)	No Cd test. Performed in 1:5 HCl.
Cd (1) Fe (1)	Cd test poor and difficultly recognizable.
Cd (1) Fe (0.1)	Good Cd test. Crystals colored light lavender.
Cd (1) Ni (1)	No Cd test.
Cd (1) Ni (0.1)	Cd crystals often tapering and in peripheral clusters.
Cd (0.1) Ag (1)	Ag precipitate masks Cd.
Cd (1) Sn (1)	No Cd test. Performed in 1:5 HCl.
Cd (0.1) Ti (1)	No Cd test. Performed in 1:5 HCl.
Cd (0.1) Zn (1)	No distinguishable Cd test.
Cd (1) Cl (2)	A satisfactory test is not obtained if the chloride ion concentration is much above 2%. Since some of the above ions were used in chloride solution (17%), the presence of the chloride rather than the metallic ion may very probably be the cause of the interference. The above tests would indicate that the mercuric and titanium ions somewhat counteract the effect of the chloride ions.
Cd (0.1) SO <sub>4</sub> (1)	Cd crystals much delayed and very poorly formed. Test only difficultly recognizable.

## Cobalt

Co (0.1) Cu (1)	No Co test.
Co (0.1) Fe (1)	All Co crystals dark, irregular, peripheral aggregates. Test poor.
Co (1) Fe (1)	All Co crystals dark, but well formed.
Co (1) Ni (1)	No evidence of Co until evaporation very far advanced and then only blue globules form.
Co (0.1) Zn (1)	No Co crystals, all Zn crystals tinged blue.

## Copper

Cu (0.1) Co (1)	Crystals of Cu form, but all colored blue.
Cu (0.1) Au (1)	Good Au test—no Cu test. Au and Cu precipitates can easily be mistaken for one another. Performed in 1:5 HCl.



Cu (0.1) Fe (1)	Many colorless, arrowhead-shaped crystals. No recognizable Cu forms.
Cu (0.1) Ni (1)	Ni spherules are all tinged green—otherwise no Cu test.
Cu (0.1) Ag (1)	Cu largely masked.
Cu (0.1) Sn (1)	No Cu test. Performed in 1:5 HCl.
Cu (0.1) Ti (1)	Cu test not recognizable. Performed in 1:5 HCl.
Cu (0.1) Zn (1)	Zn crystals all tinged purple—otherwise no Cu test.

Gold

Au—Cu	The copper and gold precipitates can be easily confused. The gold dendrites are, however, considerably browner and part of the precipitate shows a gold color in reflected light.
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Iron

Fe (0.1) Ag (1)	Ag precipitate colored brown—otherwise no Fe test.
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Nickel

Ni (1) Sb (0.1)	No Ni test. Performed in 1:5 HCl.
Ni (1) Cd (1)	No Ni test.
Ni (0.1) Co (1)	No Ni test.
Ni (1) Cu (1)	Ni globules green and easily confused with poorly formed Cu clusters.
Ni (1) Au (1)	No Ni test. Performed in 1:5 HCl.
Ni (1) Sn (1)	No Ni test. Performed in 1:5 HCl.
Ni (1) Ti (1)	No Ni test. Performed in 1:5 HCl.
Ni (1) Cl (10)	No Ni test.
Ni (1) Cl (5)	Good Ni test. The interfering effect of the Cl ion thus begins somewhere between 5 and 10 per cent.

Silver

Ag (0.1) Cu (1)	Ag precipitate masked by Cu.
Ag—Sb, Au, Sn, Ti	These elements were present only in chloride solutions and could thus not be tested in the presence of Ag.
Ag (1) Cl (0.1)	Presence of Cl inhibits the Ag test by precipitating AgCl.

Zinc

Zn (0.1) Sb (1)	Maltese crosses, black squares, some Cd-like crystals and some good Zn crosses. Performed in 1:5 HCl.
Zn (0.1) Bi (1)	Numerous formless, colorless to opaque grains and small stubby Cd-like crystals. Few Zn crosses. Poor test.
Zn (0.1) Cd (1)	No Zn test.
Zn (0.1) Co (1)	No Zn test.
Zn (1) Co (1)	Curved prisms and poorly formed crosses—all blue.
Zn (0.1) Cu (1)	No Zn test.
Zn (1) Cu (1)	Some Zn crosses all dark purple in color.
Zn (0.1) Au (1)	Maltese crosses, black squares, Cd-like crystals. Performed in 1:5 HCl.
Zn (0.1) Mn (1)	Many irregular opaque grains; some good crystals.
Zn (0.1) Hg (1)	Poor test, mainly stubby prisms, also a few good Zn crystals.
Zn (0.1) Ni (1)	No Zn test.

- Zn (0.1) Cl (15)      Zinc forms much altered; consist mainly of Maltese crosses, black squares, and many crystals that appear very similar to the Cd crystals with cavities at the ends. Since some of the cations used were present in a (17) HCl solution, the Cl rather than the metallic ion may very probably be the cause of the interference noted. 1:5 HCl does not interfere with the (1) Zn test.
- Zn (0.1) Cl (10)      Good Zn test.

#### DISCUSSION

**Cadmium:** In testing for cadmium, it is imperative to avoid a high chloride ion concentration in the drop. The numerous interferences of the chloride ion in the thiocyanate test afford a strong argument in favor of first attempting to dissolve a mineral in nitric acid before either hydrochloric acid or aqua regia is used. The major interference of cobalt is relatively unimportant since cobalt and cadmium are not common natural associates. The marked interference of iron (C, p. 128) is, however, quite a serious difficulty in view of the widespread occurrence of iron as a mineral impurity. We know of no remedy for interference by iron. The minor interference of silver is relatively unimportant (C, p. 128). Silver can be removed by potassium bichromate before testing for cadmium.

**Cobalt:** The major interference of nickel (S, p. 135) and iron (S, p. 136) and the minor interference of zinc can be remedied by the use of the cesium chloride test for cobalt (a new test to be described subsequently). The  $\alpha$  nitroso- $\beta$  naphthol test is not a satisfactory test for cobalt.

**Copper:** The purple color of zinc crystals in the presence of copper, even when no copper dendrites are formed, is often a satisfactory test for copper and one utilized by Watson as a spot test (W, pp. 25, 26). The major interference by gold can be remedied by use of the cesium chloride test for copper. However, the two cations are not commonly associated in minerals, but if they do occur together they can be separated by dissolving the mineral in nitric acid. The cesium chloride test will likewise remedy the minor interference of nickel and cobalt. When tin and titanium are in solution, the potassium iodide test for copper may be of assistance. Some of these interferences have been mentioned previously: cf. copper in the presence of cobalt (S, p. 136), gold (C, p. 250), and zinc (S, p. 130).

**Gold:** The copper and gold precipitates can be easily confused. The gold dendrites are, however, considerably browner, and part of the precipitate shows a gold color in reflected light. Where copper is present, pyridine-hydrobromic acid will give a satisfactory gold test (S, p. 154). The minimum sensitivity of the gold test with thiocyanate is 0.3 per

cent of the element. The interference tests discussed here were (contrary to general practise) run with a 1 per cent gold solution as a minimum concentration.

**Iron:** The iron test is highly satisfactory. When silver is present in solution, it should be removed by bichromate before a test is run for iron.

**Nickel:** A high chloride ion concentration will seriously interfere with the nickel test which, even under ordinary conditions, is somewhat delayed. Minor interference is offered by cadmium, cobalt, and copper. However, by using a modification of the dimethylglyoxime test, nickel can be satisfactorily ascertained in the presence of all of the aforementioned ions (W, p. 32).

**Silver:** The bichromate test is probably preferable to the thiocyanate test. However, other than the interference of the chloride ion, only copper will offer a minor interference to this test.

**Zinc:** The presence of a relatively high chloride ion concentration in dilute zinc solutions materially alters the zinc precipitate. Black squares, maltese crosses, and many prisms that are very similar to the cadmium prisms appear. Copper offers a major interference to this test although, even when no zinc crystals are present, the purple color of the copper dendrites may aid in the detection of zinc. There is no present remedy for the major interference of cobalt (S, pp. 131-132). There is likewise no remedy for the minor interference of nickel or cadmium (C, pp. 128-129).

### 3. DIMETHYLGLYOXIME TEST

#### *Individual Reactions*

A drop of reagent is added to a drop containing a (1) solution of the element in neutral or weakly alkaline solution.

- Ag No precipitate.
- As A 1 per cent solution of  $\text{NH}_4\text{OH}$  precipitates much of the arsenic as colorless octahedrons.
- Bi No precipitate.
- Cd No precipitate.
- Co No precipitate.
- Cu No precipitate in 1 per cent nitric acid solution. In 1 per cent ammonia, a strong, yellow fine-grained precipitate of grains and needles forms.
- Cr Yellowish-brown fine-grained precipitate. No precipitate in 1 per cent nitric solution.
- Fe No precipitate on adding a drop of 1 per cent  $\text{NH}_4\text{OH}$  to the iron in 1 per cent or less nitric acid. Color of drop turns brown. No precipitate on addition of dimethylglyoxime.
- Hg Precipitate of very small black grains. White in reflected light.
- Mn No precipitate.
- Ni Immediate precipitation of small pink needles.

- Pb Strong precipitate of very small black grains. White in reflected light.  
 Se No precipitate.  
 Te On addition of 1 per cent  $\text{NH}_4\text{OH}$  gives a brown to black precipitate. No precipitate from a 1 per cent nitric solution.  
 Zn On addition of 1 per cent  $\text{NH}_4\text{OH}$  gives a whitish precipitate. No precipitate in 1 per cent nitric solution.

### *Interference Reactions*

(Test performed by mixing solutions in dilute nitric acid, neutralizing with  $\text{NH}_4\text{OH}$  and adding reagent.)

#### Nickel

- Co (0.1) Ni (0.01) Presence of Co greatly delays Ni test which appears in small quantities at edge of drop as it dries. Volume of Ni precipitate is greatly lessened. Some check tests gave yellow and purple needles instead of usual red. Test not reliable.  
 Co (1) Ni (0.01) Sometimes a trace of nickel; sometimes no nickel test.  
 Fe (1) Ni (0.01) No interference if sufficient ammonia has been added to make test drop weakly alkaline.  
 Hg (0.1) Ni (0.01) Good precipitate, but needles are colored yellow to purple.  
 Mn (0.1) Ni (0.01) Good precipitate but needles colored light yellowish-pink.  
 Mn (1) Ni (0.01) Copious precipitate colored yellow to pinkish-brown. Definite color interference.  
 Pb (1) Ni (0.01) No interference if solution is weakly alkaline except that lead precipitate of black grains tends to mask the nickel.  
 Zn (1) Ni (0.01) No interference if solution is weakly alkaline except that whitish precipitate of Zn tends to mask Ni precipitate.

### DISCUSSION

Minor interferences are due to Co, Hg, and Mn. Cobalt interferes (S, p. 134) seriously when it is present in amounts greater than ten times the nickel. There is no easy satisfactory method of separating the two. The presence of either mercury or manganese changes the color of the precipitate but does not prevent its formation. No interference was noted in the presence of As, Ag, Bi, Cd, Cr, Cu, Fe, Pb, Se, Te, Cl, or  $\text{SO}_4$ .

#### 4. AMMONIUM BICHROMATE TEST

##### *Individual Reactions*

Small grains of ammonium bichromate are dissolved in distilled water until the solution is strong enough to give a good test when added to a drop of (0.1) Ag in 1 per cent nitric acid. This solution is then used to test a 1 per cent solution of the elements in 1 per cent nitric acid.

- Ag Yellow blades of silver chromate and red blades of silver bichromate.  
 As Slow formation of good octahedrons and tetrahedrons. Some colorless, some dark.  
 Bi Immediate fine-grained dark precipitate, green in reflected light. This precipitate is soluble in 1:7 nitric acid and does not reform until the drop dries to give a yellow mass, yellowish-green in reflected light.

Cd	No precipitate.
Cu	No precipitate.
Cr	No precipitate.
Fe	No precipitate.
Hg	Slow precipitation of a few black grains, yellowish-white in reflected light.
Mn	No precipitate.
Ni	No precipitate.
Pb	Immediate precipitation of fine-grained, yellowish grains, yellow in reflected light.
Se	No precipitation until drop begins to dry, then there is a very fine-grained, dark precipitate around edge of drop.
Te	Immediate fine-grained, dark precipitate.
Zn	No precipitate.

*Interference Reactions*

## Silver

As (1) Ag (1)	Slow formation of good octahedrons and tetrahedrons, colorless to dark in transmitted light, white in reflected light. No silver bichromate or chromate blades.
As (1) Ag (0.1)	Octahedrons and tetrahedrons—no silver test.
As (0.1) Ag (1)	Strong silver test.
As (0.1) Ag (0.1)	Slow formation of bladed and feathery forms at edge of drop, dark red to black color. Forms sometimes very feathery.
Bi (1) Ag (0.1)	Immediate fine-grained precipitate soluble in 1:7 HNO <sub>3</sub> , good silver test.
Cu (1) Ag (0.1)	Silver blades are small and often colored blue, but test is satisfactory.
Cr (1) Ag (0.1)	Silver blades are stumpy and often form as rounded grains. Test recognizable but not very satisfactory.
Hg (1) Ag (0.1)	Black grains, yellowish-white in reflected light, just before drop dries a few silver bichromate blades may form on edge of drop.
Hg (1) Ag (1)	Good silver test although first formed blades are dark red to black. Precipitate contains numerous black grains also.
Hg (0.1) Ag (0.1)	Irregular grains with a few small blades formed at edge of drop as it dries. Blades are dark red to black in color, red in reflected light.
Pb (1) Ag (0.1)	Heavy yellow lead precipitate partly masks later silver test.
Pb (0.1) Ag (0.1)	Immediate precipitation of lead chromate, later good silver precipitate.
Se (1) Ag (0.1)	Immediate fine-grained precipitate, no silver test.
Se (1) Ag (1)	Black grains, clumps of needles, crosses, white in reflected light. Later, a few red spherules are formed. No silver blades.
Se (0.1) Ag (0.1)	Black grains and needles, then red grains and spherules around edge of drop. No silver bichromate blades.
Se (0.1) Ag (1)	Black grains, colorless to black feathery blades, feathery clumps and crosses; later, formation of blades that are red when they begin to form, but turn black as they grow.
Te (0.1) Ag (0.1)	Fine-grained precipitate. Weak silver test of red to black blades.
Te (0.1) Ag (1)	Fine-grained precipitate, then good silver test.

## DISCUSSION

Major interferences by arsenic and selenium occur. In practise, the interference by arsenic is important; that by selenium not important because selenium is ordinarily not readily soluble in weak nitric acid.

Arsenic can be removed by ammonium molybdate. Chlorine is a major interference that must be avoided.

Minor interferences (Bi, Cu, Cr, Hg, Pb, and Te) are relatively unimportant because in each case it is possible to obtain a silver test, although the appearance of the precipitate will be greatly delayed and may differ considerably both in form and color. Where the presence in considerable amounts of any of these elements is suspected, the test drop must be observed until it dries, and any precipitate interpreted in view of the above notes. No interference was noted in the presence of Cd, Co, Fe, Mn, Ni, and Zn. Interference by Mn, Pb, and Hg are mentioned by Chamot and Mason (C, p. 338), and those of sulphuric, selenious and telluric acids and Pb by Short (S, p. 149).

## 5. CESIUM CHLORIDE TEST

### *Individual Reactions*

The reagent is applied in solid form to a drop of the element in 1:5 HCl where possible, otherwise in the solution previously mentioned.

- Sb White hexagons and stars.
- As Numerous, small, formless, late-forming peripheral grains and hexagonal plates.
- Bi Very thin colorless rhombs and knife-like prisms.
- Cd Tiny, colorless, hexagonal bipyramids.
- Co Light blue blades and prisms form around the periphery of the drop very late in the period of evaporation.
- Cu Golden yellow needles appear at edge of drop after evaporation is somewhat advanced. Long brown needles, red under crossed nicols, are also characteristic.
- Cr No precipitate.
- Au Small brown to opaque octahedra, as well as yellowish green, rectangular, anisotropic crystals.
- Fe Bright yellow blades and pyramids which appear anisotropic.
- Pb Small, colorless rhombs, crosses and plates of irregular shape with high refractive index and low double refraction. Precipitate appears in a (0.1) Pb solution from which some Pb has first been precipitated by HCl.
- Mn Colorless, highly refracting prisms and blades often in clusters. Does not form in a (0.1) solution.
- Hg Highly refracting, colorless cubes and octahedra as well as hexagonal plates and prisms with low order interference colors. Does not appear in (0.1) solution.
- Ni No precipitate.
- Se Colorless plates and formless grains. Weak in (0.1) solution.
- Ag Not soluble in a HCl solution, hence no precipitate.
- Te Honey-yellow isometric crystals, chiefly octahedra. Also hexagonal and triangular plates.
- Sn Small white octahedra and Y-shaped crystals.
- Ti Round, colorless, very late forming gray globules. Not formed in a (0.1) solution.
- Zn Colorless rhombs, branching forms, prisms and hexagonal plates showing low order interference colors form at edge of drop. Reaction very much delayed in a (0.1) solution,

Interference Chart

Element Tested for	Interfering Elements																				
	Sb	As	Bi	Cd	Co	Cu	Cr	Au	Fe	Pb	Mn	Hg	Ni	Se	Ag	Te	Sn	Ti	Zn	NO <sub>3</sub>	SO <sub>4</sub>
Sb		○	○	○	○	×	×	×	○	×	○	×	○	×	—	×	×	×	×	○	○
Bi	○	×		×	○	○	○	×	○	○	○	○	○	○	—	○	○	○	○	○	○
Co	○	○	○	○		×	○	○	○	○	○	○	○	○	—	○	○	○	○	○	○
Cu	○	○	×	○	○		○	○	×	○	×	×	○	×	—	○	×	×	×	×	×
Te	×	×	○	×	○	○	○	×	×	○	○	×	○	○	—		×	○	○	○	○
Sn	○	○	○	×	○	×	○	×	○	○	×	×	○	×	—	×		○	○	○	○

Interference Reactions

Antimony

- Sb (0.1) Cu (1) No Sb test.
- Sb (0.1) Cr (1) Crystallization much delayed. Crystals very irregular and generally unrecognizable.
- Sb (0.1) Au (1) No Sb test.
- Sb (1) Au (1) Sb crystals largely masked by Au and considerably darkened.
- Sb (0.1) Pb (1) No Sb test.
- Sb (0.1) Hg (1) Numerous long peripheral needles and smaller clusters of needles within the drop—all colorless and having weak birefringence. Many small Sb plates largely masked.
- Sb (0.1) Se (1) Crystallization much delayed. Test largely masked.
- Sb (0.1) Te (0.1) Sb crystals very small and indistinct.
- Sb (0.1) Sn (1) Sb masked by Sn precipitate.
- Sb (0.1) Ti (1) Very poor test—very few good Sb crystals.
- Sb (0.1) Zn (1) Sb weak and much delayed.

Bismuth

- Bi (0.1) As (1) Bi largely masked by As.
- Bi (0.1) Cd (1) Bi largely masked by Cd.
- Bi (0.1) Au (1) Bi slow in forming and considerably masked by Au.

Cobalt

- Co (1) Cu (1) Residue colored light green by Cu so that Co can not be recognized.

Copper

- Cu (0.1) Bi (1) No satisfactory Cu test.
- Cu (0.1) Fe (1) Cu precipitate largely masked by Fe precipitate.
- Cu (0.1) Mn (1) No Mn test.
- Cu (1) Mn (1) No good Cu test. Numerous colorless and brown needles.
- Cu (0.1) Hg (1) Hg crystals assume greenish color, but typical Cu needles absent.
- Cu (0.1) Se (1) Crystals of Se colored green, but no other Cu test.
- Cu (0.1, 1) Sn (1) No customary Cu test but peripheral clusters of long, colorless needles as well as the regular Sn test.
- Cu (0.1) Ti (1) No satisfactory Cu test.
- Cu (0.1) Zn (1) No satisfactory Zn test.

- Cu (0.1) NO<sub>3</sub> (1) Cu test much delayed.  
 Cu (0.1) SO<sub>4</sub> (1) Many bright yellow hexagonal plates, a few greenish yellow crystals, but no long brown needles.

## Tellurium

- Te (0.1) Sb (1) Te precipitate largely masked by Sb.  
 Te (0.1) As (1) Te precipitate largely masked by As.  
 Te (0.1) Cd (1) No Te test.  
 Te (0.1) Au (1) No Te test.  
 Te (0.1) Au (0.1) Te present, but largely masked by Au precipitate.  
 Te—Fe The Te test is easily confused with the Fe precipitate although it is sometimes possible to distinguish the two.  
 Te (0.1) Hg (1) Hg precipitate apparently masks Te. No Te visible.  
 Te (0.1) Sn (1) No Te test discernible.

## Tin

- Sn—Cd The Cd and Sn precipitates are very similar, but can be distinguished by the anisotropism of the Cd bipyramids as compared to the isotropic Sn octahedra.  
 Sn (0.1) Cu (1) No Sn test.  
 Sn (0.1) Au (1) Sn largely masked by Au precipitate.  
 Sn (1) Au (1) Sn present, but crystals are colored brown and are only difficultly distinguishable from the Au precipitate. The Sn octahedra are generally somewhat smaller than those of the gold precipitate and are not so highly refracting.  
 Sn (0.1) Mn (1) Sn crystals small and somewhat delayed.  
 Sn (0.1) Hg (1) Sn crystals much delayed and extremely small.  
 Sn (0.1) Se (1) Sn apparently forms readily in the presence of Se, but where Sn concentration is low, the Sn precipitate appears similar to the Se with which it might then be confused.  
 Sn (0.1) Te (0.1) Sn precipitate poor.

## DISCUSSION

Antimony: The major interference to this test is offered by gold. Where the antimony concentration is rather high, the phosphomolybdic acid spot test has been found to be satisfactory (W, p. 29). Antimony and gold are not, however, natural associates. Moreover, if the mineral is decomposed with nitric acid and then leached with cold 1:5 HCl, virtually no gold will be present in the solution. Of the elements that show minor interference, the double iodide test will remedy the effect of zinc, tellurium, chromium, lead, titanium and mercury. The only remedy that can be offered for the interference of copper, selenium and tin is the phosphomolybdic acid test, providing the antimony concentration is sufficiently high.

Bismuth: Major interference to this test is likewise offered by gold, if present. Where the concentration of bismuth is sufficiently high, the



thiourea spot test (W, p. 30) is a satisfactory substitute test, although selenium will partly interfere. Minor interference in the chloride test is shown by cadmium and arsenic. Bismuth is not a naturally occurring associate of the former; when the two are present in solution the double iodide test will be satisfactory. The interference of arsenic is more serious and one for which no remedy can be offered, where the arsenic can not be first removed by precipitation with ammonium molybdate.

**Cobalt:** This test for cobalt has not been previously described. It consists of the formation of blue cobaltous chloride crystals when the evaporation of the drop is well advanced. Only copper, which gives a green residue when the evaporation of the drop is well advanced, will interfere with the test. No remedy can be offered for the copper interference, since copper will likewise interfere with the thiocyanate test. A test that does not appear until the reagent begins to precipitate by evaporation is not, in general, regarded as a useful test. The presence of cobalt is, however, so easily recognized by the use of this test that it is believed that this test will be quite convenient where the thiocyanate test proves unsatisfactory.

**Copper:** Major interference by tin and manganese characterizes this test. The manganese interference is of no importance since it will not interfere with the thiocyanate test. When tin is present, the only possibility of obtaining a sure copper test is with potassium iodide, a test which is not highly distinctive. Of the ions that offer minor interference, those of sulphate, nitrate, and ferric are most likely to cause trouble. However, neither these three ions nor selenium and bismuth will interfere with the thiocyanate test. When zinc and titanium are present in solution, only the potassium iodide test will be positive.

**Tellurium:** The fact that iron offers a major interference to this test is indeed a very serious objection to the continued use of cesium chloride test for tellurium. The authors have tried several other tests for tellurium, but none have proved wholly satisfactory. Gold also presents a major interference, but this is unlikely to be important in testing minerals. The telluride minerals are decomposed by nitric acid with liberation of the gold as metallic particles. Leaching the residue dissolves the tellurium, thus separating it from the gold which is insoluble in 1:5 HCl. The solution will give a satisfactory test for tellurium with cesium chloride. The fact that tellurium and cadmium are not common associates makes the major interference of that element unimportant. In the presence of either cadmium or iron, the somewhat indistinctive potassium iodide test for tellurium is satisfactory. The potassium iodide



*Interference Reactions*

All of the following interference reactions were made with both elements in a 1:5 HCl solution except those for Pb, in which all the elements were in a (1) nitric acid solution, since the Pb test is normally made in nitric acid.

## Arsenic

- As (0.1) Sb (1) Arsenic precipitate alone gives very few discs at this concentration, but in the presence of Sb, the solution is colored yellow and yellow discs appear which are very similar to those formed in the Sb double iodide test.
- As (0.1, 1) Au (1) Au precipitate largely masks As, although As precipitate is present.

## Copper

- Cu—Au Very difficult to distinguish the two precipitates, although both are apparently present in all concentrations.
- Cu—Pb Cu cannot be distinguished in the presence of Pb, but may easily be distinguished by reflected light if no Pb is present and also by the fact that the Cu is not soluble in excess KI.
- Cu—Se Very difficult to distinguish the two precipitates although both are apparently present in all concentrations.
- Cu—Te Interference similar to that of Se.

## Lead

- Pb—Ag Good Pb precipitate but in plain light the precipitate is indistinguishable from the Ag precipitate. A distinction can be made in reflected light.
- Pb (0.1) Bi (1) Immediate precipitation of black fine-grained aggregate that spreads as a ring from KI grain, with development of golden yellow color in solution inside ring. Precipitate is brown to white in reflected light. No Pb test.
- Pb (1) Bi (1) Immediate black to red precipitate, red to yellow in reflected light. Glistens like Pb in reflected light and a few yellow plates may form but in general there is no satisfactory lead test.

## Mercury

- Hg (1) Se (1) Hg precipitate masked by Se precipitate.

## Selenium

- Se—Cu Very difficult to distinguish the two precipitates although both are apparently present in all concentrations.
- Se—Au Se and Au precipitates practically indistinguishable except by reflected light.
- Se—Te Se and Te tests are indistinguishable.

## Tellurium

- Te—Cu Very difficult to distinguish the two precipitates although both are apparently present in all concentrations.
- Te—Au Te and Au tests are indistinguishable.

Te (0.1) Pb (0.1, 1)	Presence of Te indicated by yellow color of solution and some brown precipitate although the indications might be overlooked.
Te—Se	Te and Se tests are indistinguishable.

#### DISCUSSION

**Arsenic:** The use of the ammonium molybdate test for arsenic avoids any interference by gold or antimony. In fact, the ammonium molybdate test is so satisfactory that none other need be considered.

**Copper:** It is very difficult to distinguish the copper, gold, selenium and tellurium tests with potassium iodide when it is not already known which one of the metals is in solution. Some difficulty will also be experienced in distinguishing the lead and copper tests unless use is made of reflected light. For this reason, whenever lead, selenium, and tellurium are in solution, the thiocyanate test should be used for copper and, when gold is in solution, the cesium chloride test is recommended.

**Lead:** The common association of silver and lead makes imperative the use of reflected light in the observation of the lead test. Where difficulty is experienced in determining whether the precipitate is silver or lead, the bichromate test for lead may be of assistance. With the bichromate test, lead is precipitated first and may be later masked by the silver precipitate if the latter is present in a sufficiently high concentration.

Bismuth seriously interferes with the KI test for lead (S, p. 144; C, p. 182) since it forms a double iodide which in the presence of lead gives a red to black, complex precipitate. Even a (0.1) solution of Bi is sufficient to mask the Pb precipitate from a (1) solution. Pb and Bi can be separated (S, p. 145) by converting them to chlorides and leaching the dry drop with water. Bi hydrolyzes to the insoluble  $\text{BiOCl}$  whereas the Pb chloride is soluble and the solution gives a good lead test with KI.

**Mercury:** Although this test for mercury is not as commonly used as many of the other tests discussed here, it is useful for testing concentrated solutions in which the thiocyanate test is unsatisfactory. The thiocyanate test for mercury is obtained by adding potassium thiocyanate and cobalt nitrate to the mercuric solution and is thus the cobalt test in reverse. Hence the interference effects of the thiocyanate test for mercury are identical with those in the same test for cobalt (see p. 956). The KI test for mercury, however, is so weak in a 0.1 per cent mercuric solution that in making all the interference tests for mercury here discussed, a 1 per cent solution of mercuric ions was used. Like the lead test, the mercuric test is highly soluble in excess potassium iodide and, moreover, according to Chamot and Mason (C, p. 146), is soluble in the

presence of excess mercuric ions although, with the concentrations used by the authors, no difficulty was experienced in this latter respect. Only selenium will interfere with the test by masking the mercury precipitate. When selenium is in solution, the thiocyanate test is satisfactory.

**Selenium:** The difficulty in ascertaining whether the test is that for selenium, gold, copper, or tellurium, has been previously mentioned. When these elements are in solution the thiourea test for selenium is satisfactory. Also the presence of selenium can be often detected by the deposit of metallic selenium (red in reflected light) that often forms when a test drop containing KI dries.

**Tellurium:** The difficulties mentioned under selenium are likewise applicable here. The presence of lead may be detected in reflected light. The fact that gold offers major interference to both tellurium tests is a very serious objection to the use of either test when gold is unavoidably present. There is, thus, a need for a satisfactory new test for tellurium to be used when gold and tellurium can not be first separated by selective leaching.

## 7. DOUBLE IODIDE TEST

### *Individual Reactions*

Potassium iodide and then cesium chloride are applied in solid form to a drop containing the element in 1:5 HCl where possible, otherwise in the solution previously mentioned.

- Sb Orange to red hexagons and stars.
- As Brown, amorphous, peripheral precipitate as well as orange to red hexagons; the latter forming slowly in a 0.1 per cent solution.
- Bi Red hexagonal plates—orange-colored when thin.
- Cd Colorless cubes—not in a 0.1 per cent solution.
- Co Blue-green peripheral prisms and rhombs.
- Cu Long, slender, colorless needles appear in addition to the normal potassium iodide and cesium chloride tests.
- Cr No precipitate.
- Au Precipitate same as from cesium chloride and potassium iodide tests alone.
- Fe Precipitate same as from cesium chloride and potassium iodide tests alone, plus (a) long, red to brown needles which are red under crossed nicols, brown to opaque crystals and yellow hexagonal plates all of which (especially the brown needles) tend to give way to (b) peripheral aggregates of splintery, colorless needles.
- Pb In addition to the normal lead iodide test there is precipitated a mat of slender white needles.
- Mn Same as CsCl test. Not present in 0.1 per cent solution.
- Hg Same as normal cesium chloride and potassium iodide tests—very faint in 0.1 per cent solution.
- Ni No precipitate.

- Se Same as normal potassium iodide and cesium chloride tests plus irregular, reddish brown to opaque crystals.  
 Ag Not soluble in HCl.  
 Te Same as normal KI and CsCl tests.  
 Sn Same as CsCl test.  
 Ti No precipitate.  
 Zn Same as CsCl test.

*Interference Chart*

Element Tested for	Interfering Elements																					
	Sb	As	Bi	Cd	Co	Cu	Cr	Au	Fe	Pb	Mn	Hg	Ni	Se	Ag	Te	Sn	Ti	Zn	NO <sub>3</sub>	SO <sub>4</sub>	
Sb		×	×	○	○	×	○	×	○	○	○	○	○	×	—	○	×	○	○	○	○	○
As	×		×	○	○	×	○	×	×	○	○	○	○	×	—	×	○	○	○	○	○	○
Bi	×	×		○	○	×	○	×	○	○	○	○	○	×	—	×	○	○	○	○	○	○

*Interference Reactions*

## Antimony

- Sb—As Arsenic gives a precipitate which, in all concentrations, is very much like the Sb precipitate. Arsenic, however, unlike Sb, gives a precipitate after the KI has been added and before the CsCl is added.
- Sb—Bi Except where one of the elements is greatly in excess of the other, Sb and Bi can, in general, be separated. The Bi test is more sensitive.
- Sb (0.1) Cu (1) No Sb test.
- Sb (1) Cu (1) Sb somewhat masked by Cu precipitate.
- Sb (0.1) Au (1) No Sb test.
- Sb (0.1) Se (1) Sb test weak and much delayed.
- Sb (0.1) Sn (1) Sb crystals small, poorly formed and somewhat delayed.

## Arsenic

- As—Sb Arsenic gives a precipitate which, in all concentrations, is very much like the Sb precipitate. Arsenic, however, unlike Sb, gives a precipitate after the KI has been added and before the CsCl is added.
- As—Bi It is difficult to distinguish between As and Bi. One means of distinction is by virtue of the fact that Bi merely gives a yellow color whereas As gives a precipitate after the KI has been added and before the CsCl is added.
- As (0.1) Cu (1) Arsenic test masked by Cu.
- As (1) Cu (1) Many As crystals, but many of the crystals are poorly formed and more brown than usual.
- As (1) Au (1) No distinguishable As test.
- As (1) Au (0.1) Faint As test.
- As—Fe When the Fe concentration is relatively high there may be some difficulty experienced in noting As.

As (1) Se (1)	No As test.
As (0.1) Te (0.1)	Many colorless As crystals are visible, but no good coloration is apparent.

## Bismuth

Bi—Sb	Except where one of the elements is greatly in excess of the other, Sb and Bi can, in general, be separated. The Bi test is more sensitive.
Bi—As	It is difficult to distinguish between As and Bi. One possible means of distinction is by virtue of the fact that Bi merely gives a yellow color, whereas As gives a precipitate after KI and before CsCl is added.
Bi (0.1) Cu (1)	Bi largely masked by Cu.
Bi (0.1) Au (1)	Bi masked by Au.
Bi (0.1) Se (1)	No Bi test.
Bi (0.1) Te (1)	Bi masked by Te.

## DISCUSSION

**Antimony:** When arsenic and bismuth are in solution with antimony and the concentration of antimony is sufficiently high (a 0.1 per cent solution gives a very weak test, a 1 per cent solution gives a strong test), the phosphomolybdic acid spot test (W, p. 29) will give a satisfactory test for antimony. The minor interference of copper, gold, selenium, and tin can perhaps be corrected by use of this reagent. Where only copper is present with the antimony, the cesium chloride test for antimony will be satisfactory.

**Arsenic:** For the major interference of antimony, bismuth, copper, tellurium, selenium and gold, the ammonium molybdate test for arsenic is satisfactory.

**Bismuth:** When arsenic and antimony are in solution (and selenium is not in solution) and when the concentration of bismuth is sufficiently high (a 0.1 per cent solution gives a good test), the thiourea spot test for bismuth (W, p. 30) will be useful. The major interference of gold can also be remedied by use of this spot test. For the minor interference of copper and tellurium, the cesium chloride test will constitute a satisfactory remedy and the thiourea test is of assistance. When selenium is in solution the cesium chloride test for bismuth can be used if necessary.

## 8. THIOUREA TEST

*Individual Reactions*

A drop of a 10 per cent solution of thiourea in distilled water is added to a drop of a 1 per cent solution of the element in 1:5 HCl, unless otherwise stated.

Ag	Reaction in 1 per cent nitric acid. Ag precipitates as a dark ring at junction of drops, soluble in excess of thiourea.
As	No reaction.
Au	No reaction.
Bi	Solution turns canary yellow, no precipitate.
Cd	No reaction.
Co	No reaction.
Cr	Solution turns faint blue color, no precipitate.
Cu	Immediate heavy, dark, fine-grained precipitate, white in reflected light.
Fe	Solution turns faint pink color, no precipitate.
Hg	Immediate precipitate of colorless needles and dark grains.
Mn	No reaction.
Ni	No reaction.
Pb	No reaction.
Sb	Solution turns faint yellow color, no precipitate.
Se	Immediate precipitation of reddish to blue-black small grains that spread as streamers throughout the drop. Brilliant red in reflected light.
Sn	No reaction.
Te	No reaction.
Ti	No reaction.
Zn	No reaction.

#### *Interference Reactions*

##### Bismuth

The interference tests for bismuth were run in a 1 per cent nitric acid solution.

Ag (1) Bi (0.1)	Silver precipitate partly masks Bi color.
Cr (1) Bi (0.1)	Yellow drop slightly greenish.
Fe (1) Bi (0.1)	Yellow drop slightly orange.
Hg (1) Bi (0.1)	Mercury precipitate partly masks Bi color.
Se (1) Bi (0.1)	Bi color not visible unless drop is filtered.

##### Selenium

Bi (1) Se (0.1)	The strong yellow color of Bi appears first. Se precipitates but color is obscured by the Bi. In strong reflected light the red selenium precipitate is sometimes visible. Test not always satisfactory.
Bi (1) Se (1)	Satisfactory test.
Cu (1) Se (0.1)	Copper precipitate dark in transmitted light; brownish in reflected light, selenium obscured.
Cu (1) Se (1)	Satisfactory selenium test.
Hg (1) Se (0.1)	Heavy Hg precipitate partly obscures red Se precipitate.
Sb (1) Se (0.1)	Part of the Sb may precipitate by hydrolysis and partly obscure the Se precipitate.

#### DISCUSSION

The thiourea test for bismuth has been mentioned by Watson (W, p. 30); the application of the test to selenium was worked out by Mr. M. H. Evans, California Institute of Technology.



The test for bismuth is carried out in a weak nitric acid solution. The yellow bismuth color is not intense but is evident for bismuth solutions containing down to 0.01 per cent bismuth. The presence of chlorides tends to inhibit the reaction. The following elements give no reaction in nitric acid and do not interfere with the bismuth test: As, Au, Cd, Co, Cu, Mn, Ni, Pb, Sn, Te, Ti, Zn. Antimony is not stable in nitric acid and hence does not interfere.

Copper and mercury offer minor interferences to the selenium test. None of the other elements studied seriously interfere.

#### 9. SODIUM BISMUTHINATE TEST FOR MANGANESE

A few grains of the reagent are added to a solution of the element in (1) nitric acid.

In a (0.1) solution of manganese, addition of the reagent colored the solution pink.

No color change took place in Ag, As, Au, Bi, Cd, Co, Cu, Cr, Fe, Hg, Ni, Pb, Sb, Se, Sn, Te, Zn.

Interference reactions, using a (1) solution of the above elements and a (0.1) solution of manganese were run. No interferences were found, except that the presence of Se appears to weaken the intensity of the reaction and make it slow in starting.

#### SUMMARY OF INTERFERENCES

In Table II, all of the elements are listed that offer major and minor interferences to the tests. Whenever the test drop of necessity contains the chloride anion and its presence alone is known to cause interference, the observed interference may be due either to the chloride anion or the metallic cation. In these doubtful cases the metallic cation is parenthesized. The table is divided into two sections: Section 1 gives the interferences among the twenty elements studied; Section 2 gives the interference among those elements which would probably be in solution in the test drop in important amounts, at the successive steps in the systematic procedure described in *U. S. Geological Survey, Bull. 825*. Hence, Section 2 contains those interferences which will be encountered in routine microchemical testing of minerals. The number of interferences in Section 2 could be further reduced in those tests performed in HCl solution by thorough leaching with nitric acid which would remove those elements soluble in nitric acid. In actual practise such thorough leaching would probably not be done until an interference was observed. Consequently these ions are left in the table.

TABLE II

React- ing Ion	Test Reagent	Interfering Ion			
		Section 1		Section 2	
		Major	Minor	Major	Minor
Ag	Amm. Bichromate	As, Se	Cu, Cr, Hg, Pb, Te	As	Cu, Hg, Pb, Te
	Pot. Merc. Thio- cyanate	Cl	Cu		Cu
As	Amm. Molybdate		Cl, Hg, Pb, SO <sub>4</sub>		Pb
	Pot. Iodide Double Iodide	Au Au, Bi, Cu, Fe, Sb, Se, Te	Sb	Bi, Cu, Fe, Sb, Se, Te	Sb
Au	Pot. Merc. Thio- cyanate	Cu		Cu	
Bi	Cesium Chloride		As, Cd, Au		As
	Double Iodide Thiourea	As, Sb Sn— —	Au, Cu, Se, Te, Hg, Se	As, Sb	Cu, Se, Te
Cd	Pot. Merc. Thio- cyanate	(Au), Cl, Co, Fe, Ni, (Sb), (Sn)	Ag, Cu, (Ti), Zn, SO <sub>4</sub>	Fe	Zn, Cu
Co	Pot. Merc. Thio- cyanate	Fe, Ni	Cu, Zn	Fe, Ni	Cu
	Cesium Chloride	Cu		Cu	
Cu	Pot. Merc. Thio- cyanate		Ag, (Au), Co, Fe, Ni, Sn, Ti, Zn		Ag, Co, Fe, Ni, Zn
	Cesium Chloride	Mn, Sn	Bi, Fe, Hg, Se, Ti, Zn, NO <sub>3</sub> , SO <sub>4</sub>	Mn, Sn	Bi, Fe, Se, Zn
	Pot. Iodide	Au, Pb, Se, Te		Se, Te	
Fe	Pot. Merc. Thio- cyanate		Ag		Ag
Hg	Pot. Iodide	Se		Se	
Mn	Sodium Bismuth- inate		Se		

TABLE II (Continued)

Reacting Ion	Test Reagent	Interfering Ion			
		Section 1		Section 2	
		Major	Minor	Major	Minor
Ni	Dimethylglyoxime Pot. Merc. Thiocyanate		Co, Hg, Mn		Co, Mn
		(Au), Cd, Cl, Cu, (Sb), (Sn), (Ti)	Co	Cu	Co
Pb	Pot. Iodide	Bi	Ag	Bi	Ag
Sb	Cesium Chloride	Au, Te	Cr, Cu, Hg, Pb, Se, Sn, Ti, Zn	Te	Cu, Hg, Se, Sn, Zn
	Double Iodide	As, Bi, Cu	Au, Se, Sn	As, Bi, Cu	Se, Sn
Se	Pot. Iodide Thiourea	Au, Cu Te	Cu, Hg	Cu, Te	Cu
Sn	Cesium Chloride	Au, Cd, Te	Cu, Hg, Mn, Se		Cu, Mn
Te	Cesium Chloride	Au, Fe	As, Cd, Hg, Sb, Sn	Fe	As, Hg, Sb
	Pot. Iodide	Au, Cu, Pb, Se		Cu, Se	
Zn	Pot. Merc. Thiocyanate	Cl, Co, Cu	(Au), Bi, Cd, Hg, Mn, Si, (Sb)	Cu	Cd, Mn

CONCLUSIONS

The series of tests discussed constitutes a large percentage of all the reactions commonly used in the microchemical identification of the ore minerals. It is hoped that the results obtained will show the dangers inherent in the present systematic scheme and also demonstrate the necessity of carrying out similar interference tests on any new reagents proposed for use.

It has already been pointed out that the number of interferences can be materially reduced by selective leaching of the decomposed mineral residue. This method must be applied with caution, however, because many of the metals that are not soluble in large amounts in a given acid are, nevertheless, sufficiently soluble to go into solution in small amounts after repeated leaching, and often only small amounts of a metal are needed to cause serious interference.

All of the foregoing interferences have been ascertained empirically with little regard to the fundamental chemical causes for such reactions. Many of the interference reactions can be satisfactorily explained by known chemical principles. For example, the interference of the chloride ion with the cadmium test is probably due to the reversible reaction whereby cadmium (and many heavy metals) and chloride ions combine to form negatively charged chloride complexes such as  $\text{CdCl}_4^{-2}$  and  $\text{CdCl}_6^{-4}$ . In many cases the major trend of such reversible reactions is toward the formation of complex ions which will not give the desired precipitate with the reagent. Whether the reversible reaction tends to go in the direction of the complex ions or in the direction of the simple anion and cation, depends largely on the relative concentration of each element in solution. The effect of a variation in concentration is to cause the amount of a given simple ion present in solution to vary within wide limits. What the available concentration of a given simple ion will be in a given solution of known concentration can be ascertained if the ionization constant of the two ions is known. Many such ionization constants have been determined experimentally. It would thus seem that the most logical method to determine elemental interference would be by the use of the ionization constants to determine the availability of the simple reacting ion in each specific case. The facts that (1) the availability of each ion is dependent on concentration; (2) the constants for all common combinations of anions and cations are not known; (3) the use of such constants becomes quite complex when more than two ions are in solution; (4) and in general microchemical work the exact concentration of the test solution is not known, make it considerably more satisfactory to attack the problem empirically.

However, a knowledge of the chemistry of such solubility and ionization factors is often most useful in predicting qualitatively what effect the mutual presence of two elements in solution may have upon the desired reaction. Thus, because the chloride ion tends to form chloride complexes with many of the metals, whereas the nitrate ion does not form nitrate complexes, it is always advisable to attempt first to dissolve a given mineral in nitric acid and carry out the possible tests before the chloride ion is introduced into the solution. However, because of the many uncertainties involved, the most satisfactory method of quantitatively determining interferences is by empirical methods.

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