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THE ELEMENTAL ANALYSIS OF AN ALLOY: AN ANALYTICAL SCHEME TO EMPHASIZE CATION CHEMISTRY

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ABSTRACT: The analytical scheme begins with a weighed, 50 to 75 mg alloy sample. Experimentally, eleven elements, Sn, Pb, Ag, Fe, Mn, Mg, Cu, Ni, Al, Zn, and Cr, can be detected and semi-quantitatively estimated in the sample. Separation of the constituents is based upon their oxide properties, control of their oxidation states, and their specific complexation chemistry. Neither hydrogen sulfide nor the sulfide ion is used in this procedure. The presence of as little as 0.5 mg of an element in the sample is easily detected and estimated.

INTRODUCTION

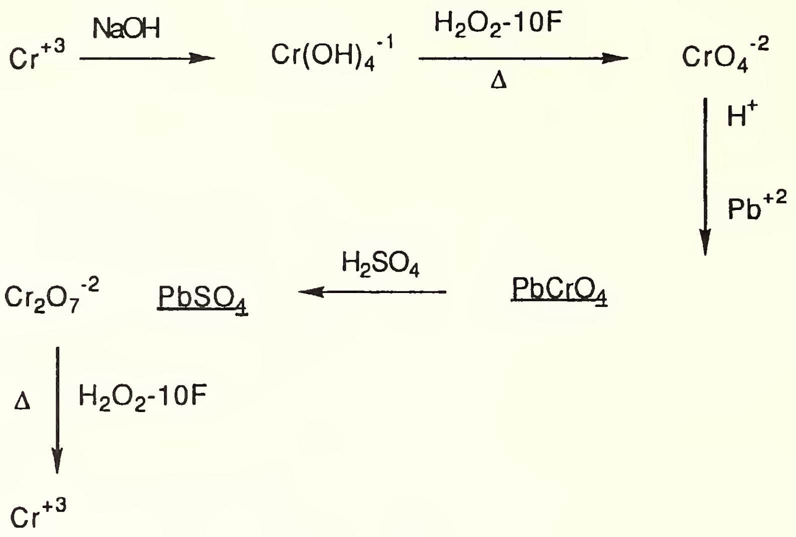
Qualitative inorganic analysis was formerly offered as a separate course during the training of a chemist. As late as 1950, 78% of the colleges (based on a sample size of 160) offered a separate course in qualitative analysis (American Chemical Society, 1950). In 1966, Kron reported that only 17% (based on a sample size of 413) offered a separate course in qualitative analysis; the remaining 83% of the colleges offered qualitative analysis as part of the second semester of the introductory chemistry course. Kron's study is the most recent survey of the place of qualitative analysis in the chemistry curriculum. In the second group of colleges, 11% demanded less than six weeks of laboratory work in qualitative analysis. In some schools, even though no formal scheme of qualitative analysis was used, the students performed qualitative analytical exercises (e.g., Frank, 1957; Thompson and Bixler, 1971; Handler, *et al.*, 1982).

When qualitative inorganic analysis is offered in general chemistry, the net result seems to be a less critical examination of the subject. In the majority of cases, the scheme of qualitative analysis that is studied consists of idealized procedures involving solution samples which have been compounded to eliminate interfering substances and to contain approximately the same amounts of the constituent species. The American Chemical Society survey (1950) noted that a marked tendency exists to omit Bi, Mg, Mn, and Sr and to a lesser extent, As, Sb, and Sn from the cation scheme in the general chemistry laboratory.

RATIONALE

Advances in analytical chemistry as a result of modern technology that allow for the use of non-destructive methods to analyze complex mixtures make the traditional scheme of qualitative inorganic analysis obsolete. However, to employ some spectroscopic methods, it is necessary to chemically remove certain interfering constituents by quantitative analytical procedures prior to their analysis. Moreover, this scheme of analysis has pedagogical merit for the same reasons that are stated in the literature by Swift (1950), Freiser (1957), and Cole and Waggoner (1983):

SOME REACTIONS OF CHROMIUM



Dilute to 10 mL and measure the % Transmittance at 590 nm. Measure % T of Chromium (III) stock solution (0.125 M), 2.0 mL diluted to 10 mL. Compare percentage recovery.

Figure 1. An outline of the experiment on chromium chemistry.

1. The student studies an analytical scheme. Real substances, metallic alloys, are analyzed. The use of alloys presents a challenge that prepared solution unknowns do not. Otto and Otto (1939) reported that the success rate for reporting cations in solution unknowns is 83.3% (based on a sample size of 13,395) and that the success rate drops to 73.8% (based on a sample size of 6,807) using solid unknowns.
2. The analysis of a small sample, 50 to 75 mg, provides an impetus for developing good laboratory technique.
3. The student sees descriptive inorganic chemistry in action. In this scheme, group separations are based in large part upon the oxide properties of the elements, the control of their oxidation state during the analysis, and the complexation chemistry of the individual elements.
4. The semi-quantitative estimation of the amount of each constituent element in the alloy creates an awareness of the importance of the concept of material balance throughout the procedure. The student does stoichiometric calculations using balanced chemical equations, which should give relevance to the importance of numbers in chemistry.
5. Performing the analytical scheme places the student in an active learning environment. Students make decisions and reach conclusions that are derived from their individual observations.

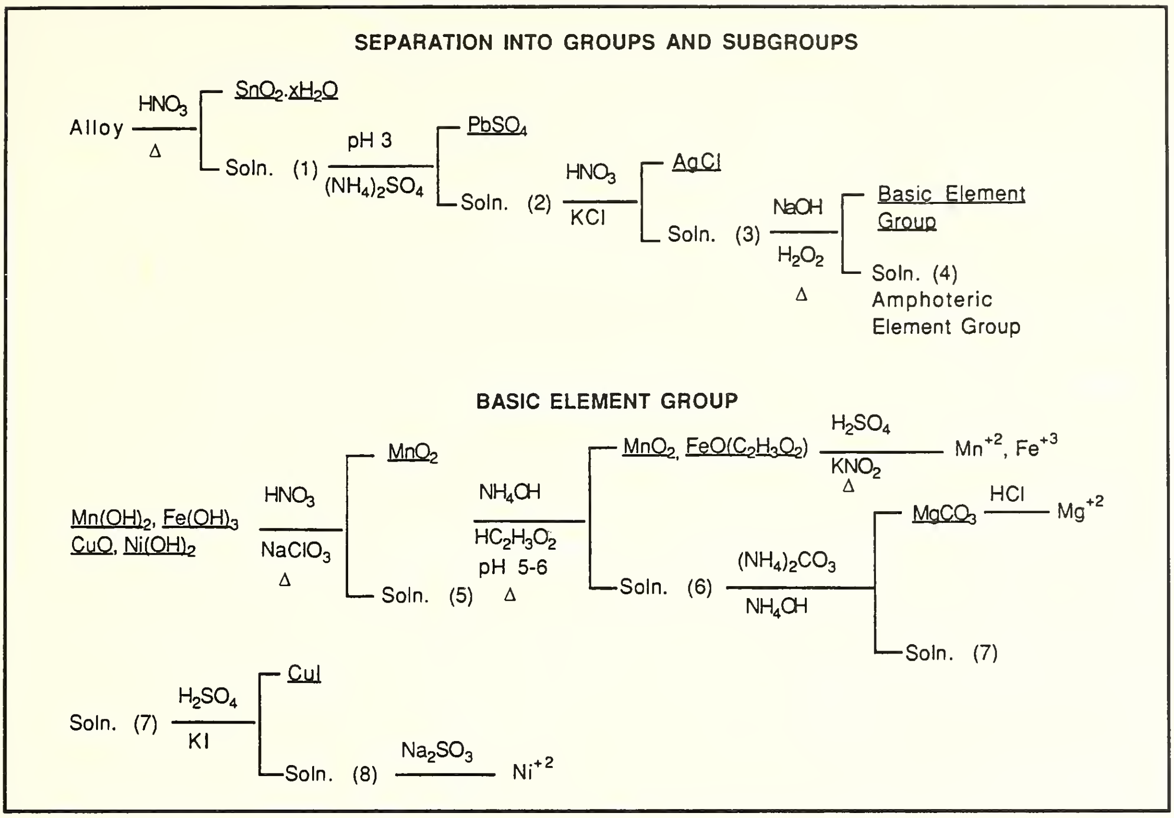


Figure 2. The separation of the elements into groups and subgroups.

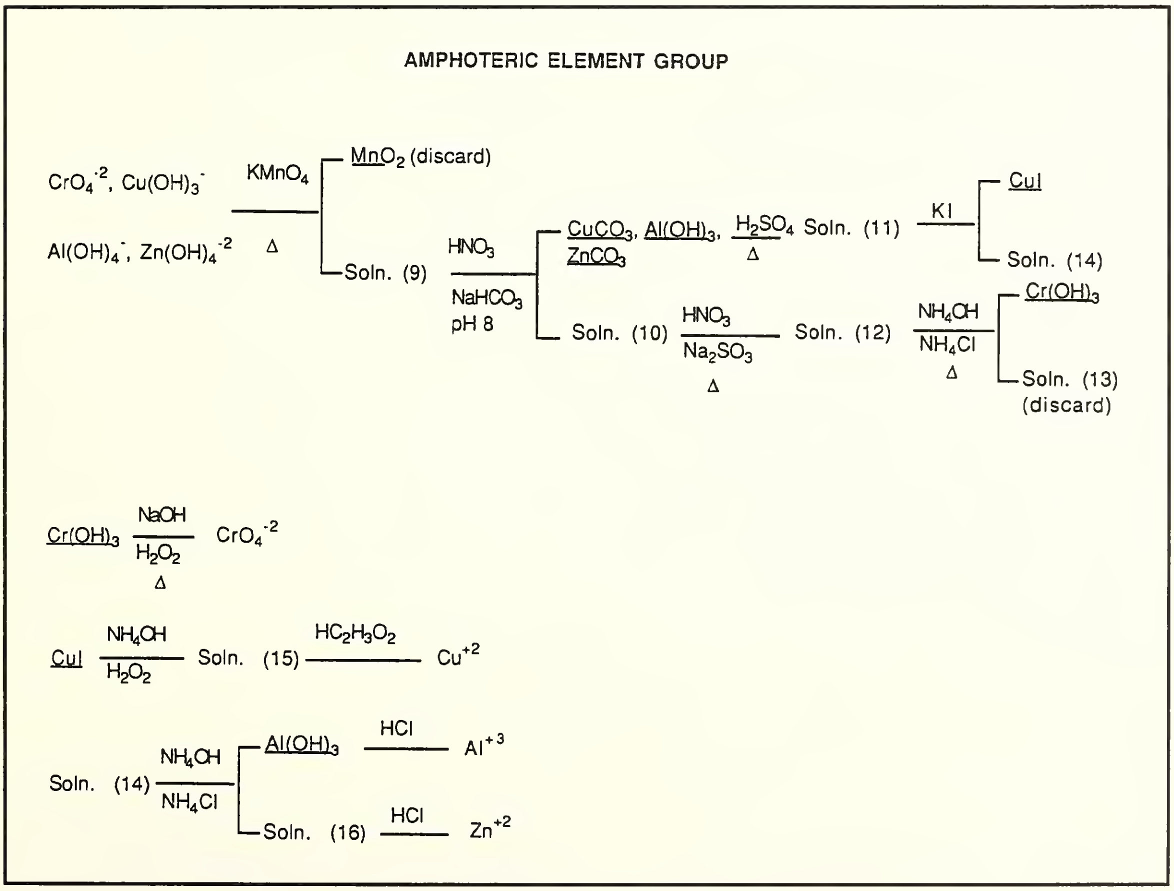


Figure 3. Separation of the amphoteric group into subgroups.

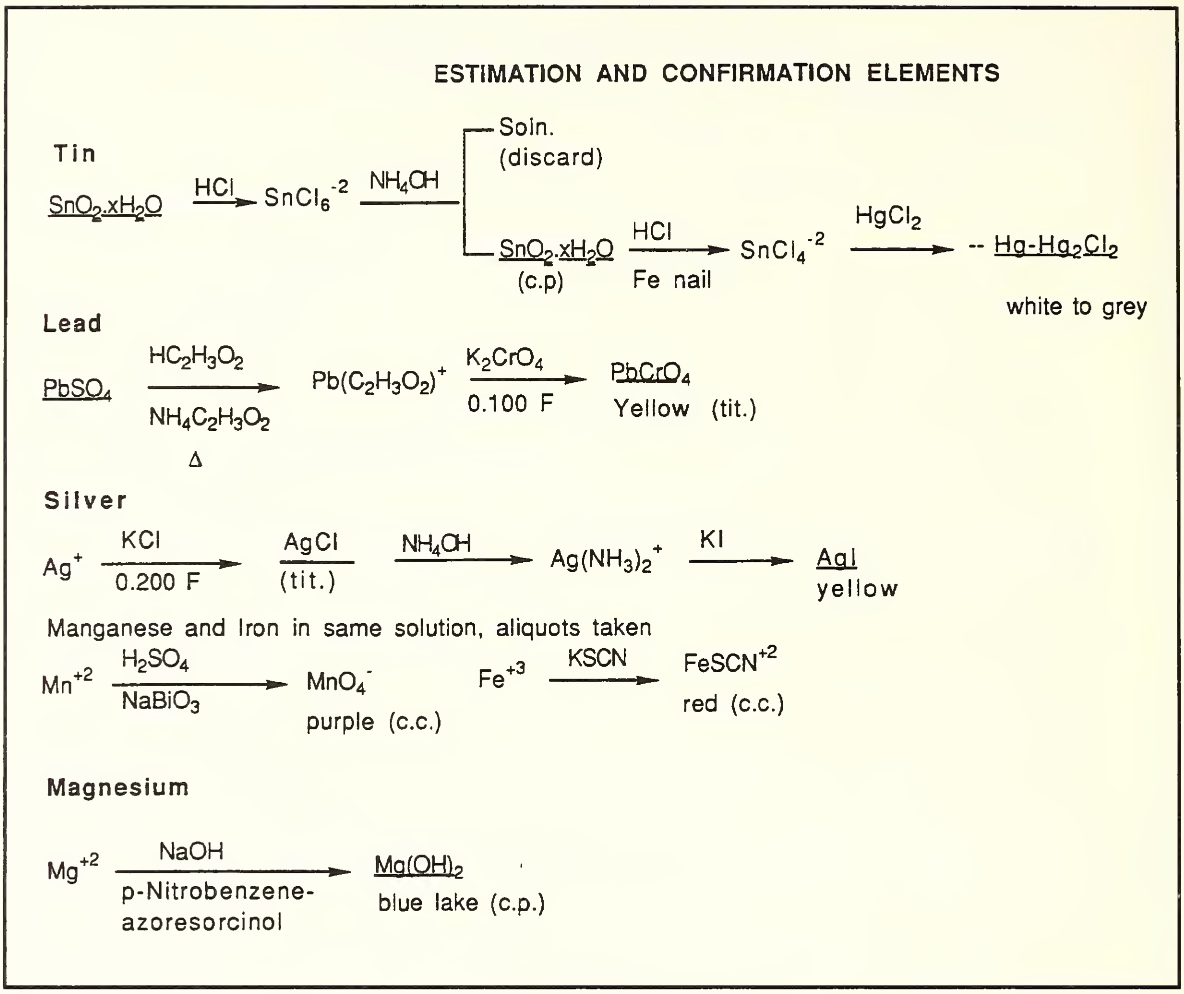


Figure 4. The estimation and confirmation of the elements.

In connection with the last point, the study by Shamal and Stavy (1986) is worth citing. Prior to studying the behavior of electrolyte solutions and ionic equilibria, a class of 71 high school seniors was divided into two cognitively matched groups. The division was based on the results of the paper and pencil test reported by Lawson (1978) and the academic performance of the students during their first semester chemistry course. One group, the experimental group, completed a 25 hour course in qualitative analysis before studying the topics of ionic equilibria, while the second group, the control group, did not. Both groups studied two chapters on ionic equilibria simultaneously. Five separate tests were given over these chapters. Their tests were graded by two other high school chemistry teachers. The average scores on the tests were 70% for the control group and 82% for the experimental group, suggesting that a laboratory experience stressing chemical analysis preceding its theoretical study enhances understanding and mastery of the principles involved.

THE ANALYTICAL SCHEME

Of the many qualitative group separation procedures in the literature (e.g., Rich (1984) cites 18), only the text by Swift and Schaefer (1962) presents a procedure involving the separation, identification, and estimation of 24 elements in a solid sample. Their scheme is an adaptation of the procedure developed at the California Institute of Technology for the National Research Committee in 1942 for 34 elements (Swift and Niemann, 1954). The

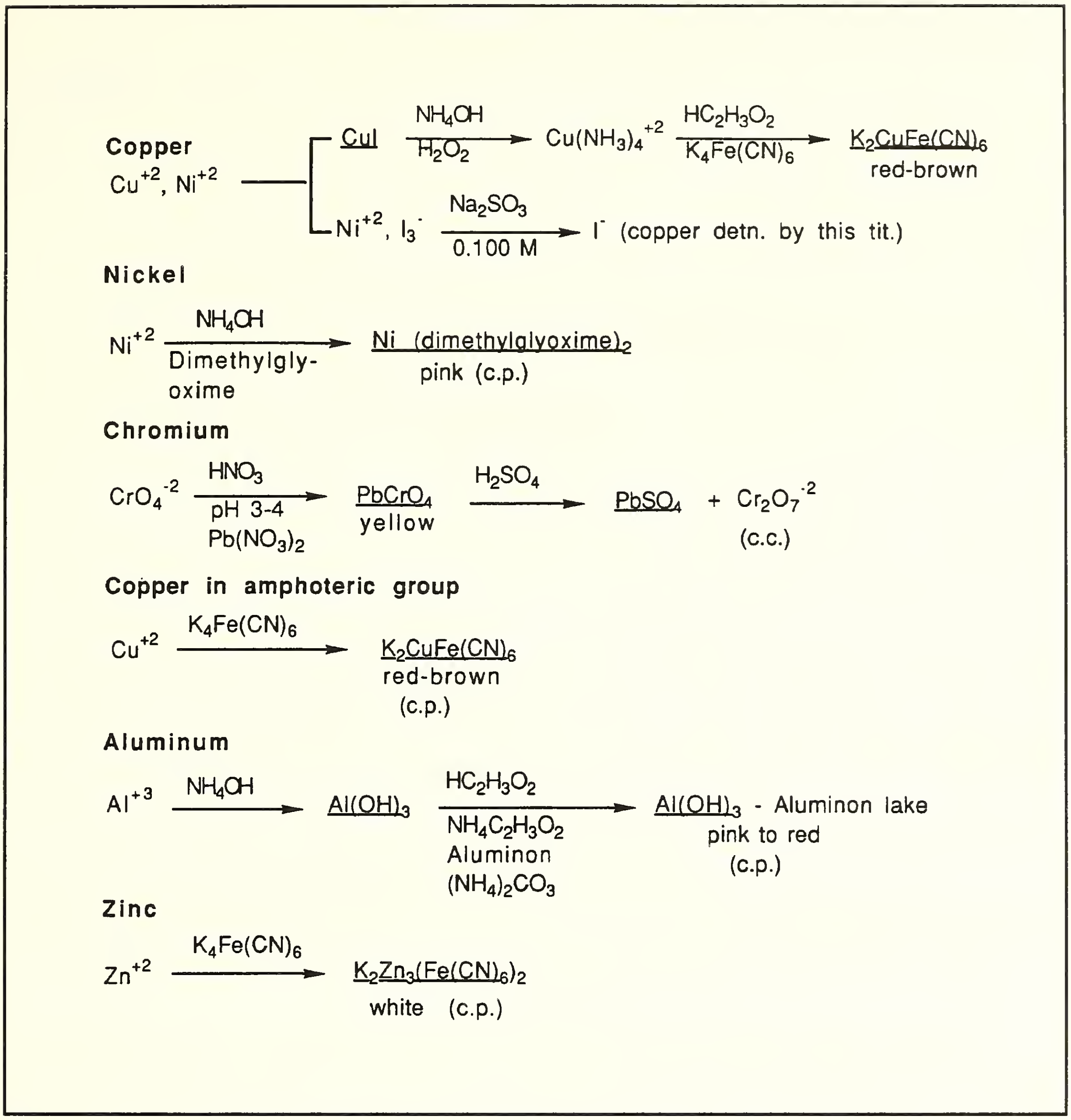


Figure 5. The estimation and confirmation of the elements (continued).

analytical scheme described in this paper is a modification of the scheme developed by Swift and Schaefer. The use of hydrogen sulfide or the sulfide ion is eliminated in the separation and estimation procedures by using metallic alloys as unknowns. In addition, sodium bicarbonate replaces carbon dioxide during the separation of the amphoteric elements in this procedure. With a 50 mg sample, a trained chemist can detect, with an accuracy of 10%, any element that is present in an amount greater than one percent. Of course, freshman students are not trained chemists. However, the better students will find those constituent elements that are present in an amount greater than three or four percent with an accuracy of between 25% and 50%. In six, three-hour laboratory periods, a student is able to analyze two to three alloy samples.

Initially, each student performs a preliminary exercise that covers some of the chemistry of chromium. The experimental design is adapted from the material included in the Swift and Schaefer (1962) text. The preliminary exercise introduces important techniques, such as the quantitative separation of a precipitate from a centrifugate using a Pasteur dropping pipet and the quantitative dilution of a solution using a 10-mL graduate. The experimental calculations employ the concept of material balance to ascertain the results which

Table 1. Analysis of a German silver and a brass alloy.

Element	Percentage Present	Percentage Found: Faculty	Percentage Found: Student Average
German Silver			
Cu	63.3	57	41
Ni	15.9	12	6.4
Pb	0.30	absent	absent
Fe	0.20	0.23	trace
Mn	0.23	trace	absent
Zn	20.1	14	8.6
Brass			
Cu	86.2	83	70
Sn	4.7	2.9	trace*
Pb	4.7	3.4	1.8
Zn	3.6	2.5	absent

* Reported by only one student.

can be expected using a series of quantitative reactions. Figure 1 outlines the experiment, which is performed in 15-mL test tubes. Those students with good laboratory technique recover 75% to 90% of the Cr. This recovery rate represents a loss of between 1.3 mg and 3.3 mg.

To provide a sound introduction to a real analytical procedure and to avoid the use of the sulfide ion in the chemical separations, the unknowns are alloys that may contain Sn, Pb, Ag, Fe, Mn, Mg, Cu, Ni, Al, Zn, and Cr as major constituents. Suitable analyzed samples (brass, silver, Dow metal, monel metal, German silver, steel, and zinc-aluminum alloys) can be purchased from Thorn Smith Laboratories (7755 Narrow Gauge Road, Beulah, Michigan 49617). Devarda's alloy and lead-tin solders also make suitable unknowns. The chemical reactions may be performed in a 50-mL Erlenmeyer flask or a 15-mL test tube. Pasteur dropping pipets with bulbs are used to separate precipitates from their centrifugates. A calibrated Pasteur pipet (30 to 35 drops/mL) is used in titrations and to measure known quantities of the element being determined from a standard solution for comparative purposes. Quantitative dilutions are made using either a 10-mL or a 25-mL graduate.

Figures 2 through 5 outline the analytical scheme. At the point where the amount of each element is estimated, abbreviations are used to refer to (1) a comparison of the precipitate size of the compound of the element with that formed from a known amount of the element (c.p.), to (2) a comparison of color intensity from a complex of the element in a fixed volume of solution that is matched to that produced by a known amount of the complex of the element in the same volume of solution (c.c.), or to (3) the titration of some chemical species which can be related to the amount of reagent (tit.).

RESULTS

Table 1 lists the results that were obtained using this analytical scheme on two alloys, German silver and brass. Each alloy was analyzed by one of the authors and by a pair of freshman. Predictably, the student results were less precise than those of the faculty member. However, the students did find the major constituents. One result does not appear in the table. During a faculty member's analysis of the German silver, 3.3 mg of Cr^{+3} were added after the dissolution of the solid. The resulting solution was carried through the analytical procedure, and 2.7 mg of Cr was recovered.

CONCLUSIONS

The demands that are associated with this analytical procedure will increase student confidence in their ability to do laboratory work. By introducing the scheme during the first semester laboratory, there should be carry over to other laboratory courses. The challenge of decision making during the analysis will stimulate cognitive awareness within the student. Chemical reactions will be demonstrated by the student doing the chemistry. The stoichiometric calculations become real rather than contrived. Whether the scheme is relevant or not to "real world" analysis, it does require that students do chemistry early in their chemical education. For this reason, it should be valuable for use in an advanced high school chemistry course as well as in an introductory college course.

Copies of the procedures for the analytical scheme and the preliminary exercise on the chemistry of chromium can be obtained from the authors. Included will be a list of reagents with their concentrations that are required to carry out the analytical procedures.

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