work, and their presence or absence noted among the results. If present in little more than traces that knowledge alone may suffice, for it is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0.02 or 0.06 per cent. In the tabulation of analyses a special note should be made in case of intentional or accidental neglect to look for substances which it is known are likely to be present. Failure to do this may subject the analyst to unfavorable criticism when at some future time his work is reviewed and the omissions are discovered by new analyses.

Finally, whenever possible, a thorough microscopical examination of the rock in thin section should precede the chemical analysis. This may be of the greatest aid to the chemist in indicating the presence of unusual constituents or of more than customary amounts of certain constituents, whereby, possibly, necessary modifications in the analytical procedure may be employed without waste of time or labor.

ELECTROLYTIC SEPARATIONS.

By Edgar F. Smith.

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FREUDENBERG published an article recently entitled "Über die Bedeutung der elektromotorische Kraft für elektrolytische Metalltrennungen" (*Zeit. für phys. Chemie.*, **12**, 97), in which are facts of great importance to all interested in the determination and separation of metals in the electro-chemical way. Some statements, however, have been made by Freudenberg to which I feel it my duty to reply. I discover upon p. 116, for example, these lines: "Auch gelingt eine Trennung (Kupfer) von Kadmium, welche bisher nur bei Gegenwart von Saltpetersäure möglich schien, vortrefflich, wenn man die Lösung mit 10–20 cc. verdünnter Schwefelsäure versetzt und mit einer Spannung von 2 Volt elektrolysiert. Das Kupfer wird rasch und völlig kadmium-freigefällt." This very separation was carried out successfully three years ago by Smith and Frankel (*Am. Chem. J.*, **12**, 104–112 and *Ber. d. Chem. Ges.*, **23**, *Ref.* 413) as will be observed from the literature references and the examples that follow:

1. To a solution containing 0.1975 gram copper and 0.1828 gram cadmium were added ten cc. of sulphuric acid (sp. gr. 1.09) and then 100 cc. of water. A current that liberated 0.3 cc. of electrolytic gas per minute acted upon the above mixture for twelve hours. The precipitated copper weighed 0.1968 gram.

2. A second experiment made under analogous conditions, except that the volume of sulphuric acid equaled fifteen cc. gave 0.1975 gram copper.

Freudenberg, while recognizing the fact that Smith and Frankel by electrolyzing solutions of metallic double cyanides effected many separations, seems not to be fully acquainted with all that has been achieved in this direction. Thus upon p. 113 he speaks of the separation of mercury from copper and alludes to the early statement of Smith and Frankel that if the quantity of copper exceeded twenty per cent. of the mercury the separation would not be satisfactory. This is true, but if Freudenberg had examined the literature that appeared later from this laboratory he would have found that Smith and McCauley (*J. Anal. Chem.*, **5**, 489 and *Ber. d. Chem. Ges.*, **24**, 2936) observed that "it is not only possible to separate these metals (mercury and copper) completely when present together in equal amounts, but even when the quantity of the copper is twice that of the mercury. In brief, the separation is as readily and accurately made as that of any other metal, *e. g.*, zinc from mercury. Furthermore, the presence of zinc, nickel, or other metals, in no wise, influences the separation of mercury from copper." I welcome, therefore, the results of Freudenberg's experiments with mercury and copper as confirmatory of those published by Smith and McCauley.

The observation of Freudenberg (p. 114) relative to the removal of gold when precipitated directly upon platinum will be found to be antedated by reference to *J. Anal. Chem.*, **5**, 204.

As to the criticism made upon p. 117, in reference to the separation of bismuth from copper in the presence of potassium cyanide and citric acid I would only add that Smith and Frankel made numerous separations of these two metals in this way. Their results were highly satisfactory. It is true that

they never used quantities of bismuth exceeding 0.1 gram. The dishes in which the decompositions were made were large and offered ample surface so that the bismuth deposit was in every case satisfactory.

The separation of copper from arsenic, in ammoniacal solution, as outlined on p. 118 of Freudenberg's article, has already been successfully made by McCay (*Chem. Zeitung*, **14,** 509) and by Smith and Frankel (*Am. Chem. J.*, **12,** 428).

Again upon p. 122 Herr Freudenberg confirms an early observation made by Smith and Frankel in reference to their inability to completely separate cadmium from nickel in cyanide solution, but he is apparently ignorant of a later series of experiments by these same chemists in which they give proof that cadmium and nickel in cyanide solution can be separated in the electrolytic way if caustic alkali be added to the solution undergoing electrolysis. An example will illustrate:

A solution, containing 0.1723 gram cadmium, 0.1600 gram nickel, 2 grams of caustic potash, 2.5 grams of potassium cyanide to which 150 cc. of water had been added, was electrolyzed with a current that gave 2.2 cc. of electrolytic gas per minute. The precipitated cadmium did not contain nickel; it weighed 0.1723 grams (*J. Anal. Chem.*, **6,** 87, and *Ber. d. Chem. Ges.*, **25,** 784).

Freudenberg correctly adds on p. 124 that "Die Cyanverbindungen * * * * * * haben jedoch unsere Trennungs methoden bedeutend erweitert." This is evidenced by the many separations that have been effected in this laboratory in solutions of such compounds, *e. g.*

Cadmium from zinc, arsenic, tungsten, molybdenum, osmium, nickel, and cobalt; *gold* from palladium, platinum, copper, cobalt, zinc, and nickel; *mercury* from copper, zinc, nickel, cobalt, palladium, arsenic, tungsten, molybdenum, platinum, and osmium; and *silver* from copper, zinc, nickel, cobalt, arsenic, tungsten, molybdenum, platinum, and osmium.[1]

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[1] *Am. Chem. J.*, 11, 352, 264; 12, 428; 13, 417; *J. Franklin Inst.*, Dec., *1889*; *J. Anal. Chem.*, 5, 489; 6, 87.