Summary.

As a result of this investigation the following facts have been established.

The preparation of cesium bromate is probably best carried out in acid solution.

Cesium bromate is a definite crystalline salt with no water of crystallization. Occluded water causes decrepitation.

Its melting point (not as yet determined) is above that of potassium bromate. After melting, it soon decomposes, giving a large amount of oxygen, and leaves a bromide.

The solubility of cesium bromate is 4.53 g. in 100 g. of water at 30°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY.]

THE ELECTRO-ANALYTICAL SEPARATION OF NICKEL (COBALT) FROM ARSENIC.

BY N. HOWELL FURMAN.

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Introduction.

This investigation was undertaken at the suggestion of Dr. L. W. McCay, who first demonstrated the possibility of separating copper from quinquivalent arsenic in ammoniacal solution by means of the electric current.[1] A number of years ago he attempted the simultaneous separation of nickel and cobalt from arsenic by a similar method, but found that the results were always high, owing to the presence of arsenic in the deposits. The materials which he used in these investigations were specimens of smaltite and safflorite (arsenides of cobalt) which contained nickel.

The author has studied the action of the electric current upon ammoniacal solutions containing alkali arsenates and nickel alone, and finds that the nickel deposits are free from arsenic. On the other hand, when cobalt is deposited from an ammoniacal solution containing arsenates the deposit invariably contains arsenic in amounts ranging from 6.0–12.0 mg. per 0.1 g. of cobalt. If the 2 metals are deposited simultaneously they may or may not contain arsenic, for its presence depends upon the relative amounts of nickel and cobalt, and upon the absolute value of the concentration of the cobalt. For example, with a total volume of 100 cc. and a cathode surface of 55 $\overline{\text{cm}}^2$., the deposits were found to be free from arsenic when the relative amounts of the metals were 2.5 or more parts of nickel to one part of cobalt by weight, and the total weight of the mixed metals deposited was 0.1 g. When the 2 metals were present in a 1 : 1 ratio, from 0.5 to 1.0 mg. of arsenic was found in a 0.1 g. deposit of the mixed metals. If the concentration of the cobalt is increased, while the

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[1] McCay, *Chem. Ztg.*, 14, 509 (1890).

cathode surface is kept constant, it becomes increasingly more difficult to prevent the deposition of arsenic with the cobalt-nickel alloy. The separation described in this paper, therefore, finds practical application in the analysis of arsenical nickel ores in which cobalt *may be present*, but only in *small amounts*.

A detailed study of the electrolysis of ammoniacal solutions containing cobalt and alkali arsenates is in progress, and the results will be presented in a subsequent communication. Heretofore the electrolysis of alkaline solutions containing arsenates has not exhibited a reducing action upon the arsenic acid; upon this fact Covelli[1] has based a sensitive method for the detection of arsenious in the presence of arsenic compounds.

A search of the literature revealed the fact that the possibility of separating nickel from arsenic by the electrolysis of ammoniacal solutions containing the 2 elements was mentioned briefly in an early contribution from the Mannsfeld'schen Ober-Berg und Hütten-Direktion in Eisleben.[2] No experimental results were published, nor was the influence of cobalt upon the separation mentioned. Later observers either misinterpret or ignore this work. Thus Schweder[3] states, "The presence of *small* amounts of arsenic is not harmful in the electrolytic precipitation of nickel, according to experiments made in the Mannsfeld'schen Ober-Berg und Hütten-Direktion in Eisleben." Numerous later communications consulted all advise the removal of the arsenic by hydrogen sulfide before the deposition of the nickel.[4]

Experimental Part.

Solutions of nickel sulfate were prepared as needed by weighing out suitable quantities of hydrated nickel sulfate. The iron present was removed by repeated precipitations with ammonium hydroxide, and the resulting solution was diluted to a convenient volume. The solutions were standardized by precipitating the nickel in 25 cc. portions from ammoniacal solution by means of the electric current.[5] The material used

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[1] Covelli, *Chem. Ztg.*, 33, 1209 (1909).

[2] *Z. anal. Chem.*, 11, 14 (1872). "Attempts to obtain the nickel content of niccolite (Kupfer-Nickel) gave very satisfactory results. They prove that the separation of the arsenic need not precede the electrolytic estimation of the nickel, for one obtains the same results as if the arsenic had been previously removed. When the nickel deposited on the platinum, in the former case, is brought into the Marsh apparatus scarcely a trace of arsenic can be found."

[3] Schweder, *ibid.*, 16, 344 (1877).

[4] The extended list of references in "Electro-Analysis" by E. F. Smith, 1912 Ed., p. 126, many additional references cited in "Die Bestimmungsmethoden des Nickels und Kobalts," by H. Grossmann, as well as other communications listed in *Chemical Abstracts*, Vols. 1–12, were consulted.

[5] The details given in Smith's Electro-Analysis, p. 127 were followed closely. Stationary electrodes were used, the cathode being a platinum cone in the analysis of solution No. 1. and a Winckler platinum gauze in the case of solution No. 2.

was examined qualitatively and found to contain only a trace of cobalt.

NICKEL FOUND PER 25 CC. OF SOLUTION.

	G.	G.	G.	Average.
Solution No. 1	0.1029	0.1026	0.1027	0.1027
Solution No. 2	0.1782	0.1784	0.1783	0.1783

Test Separations.—In making test separations, aliquot portions of a standardized nickel sulfate solution were placed in a suitable vessel. Known amounts of arsenic were introduced, either by weighing out portions of previously analyzed di-hydrogen potassium arsenate (KH_2AsO_4), or by pipetting out aliquot portions of a solution of this salt.

Each solution electrolyzed contained 2 g. of ammonium sulfate and 15 cc. of ammonium hydroxide (sp. gr. 0.90) in a total volume of 100 to 125 cc. The current was allowed to act overnight (10 to 12 hours). The nickel was deposited upon a platinum cone, gauze or dish. The results of these separations are summarized in Table I.

TABLE I.

	Arsenic taken. G.	Nickel taken. G.	Current $N. D_{100}$. Amp.	Voltage.	Nickel found. G.	Difference. G.
1	0.0892	0.1027	0.46	3.3	0.1022	—0.0005
2	0.0849	0.1027	0.46	3.3	0.1028	+0.0001
3	0.0846	0.1027	0.55	4.2	0.1030	+0.0003
4	0.0899	0.1027	0.40	3.8	0.1030	+0.0003
5	0.1214	0.1027	0.55	3.5	0.1031	+0.0004
6	0.1072	0.2054	0.61	3.8	0.2055	+0.0001

After the nickel had been deposited and weighed the deposits were dissolved in nitric acid. The solutions of deposits 1 to 3 were combined, also those of deposits 4 to 6. The 2 resulting solutions were evaporated to dryness, the residues were taken up in as little nitric acid as possible, made ammoniacal and treated with magnesia mixture. After the solutions had been well shaken they were allowed to stand for some time but no crystals of magnesium ammonium arsenate were deposited. In both cases the introduction of 2 cc. of a standard arsenate solution (= 0.1 mg. of arsenic) gave an unmistakable precipitate of magnesium ammonium arsenate which could be converted into brown silver arsenate.

The Separation and Estimation of Both Nickel and Arsenic.

It is possible to estimate the amount of arsenic after the removal of the nickel, as the results in Table II will serve to show. The mode of procedure and conditions during electrolysis were similar to those described in the preceding section. After the removal of the nickel the arsenic was weighed in the form of magnesium pyroarsenate,[1] or as arsenic pentasulfide.[2]

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[1] Levol's method was used. Treadwell-Hall, "Quantitative Analysis," **1914**. pp. 206–208,

[2] Method devised by L. W. McCay, *Am. Chem. J.*, 9, 174 (1887).

TABLE II.

	Nickel taken. G.	Nickel found. G.	Difference. G.	Arsenic taken. G.	Arsenic found. G.	Difference. G.
1..........	0.1783	0.1785	+0.0002	0.1623	0.1614[1]	—0.0009
2..........	0.1783	0.1784	+0.0001	0.4060	0.4071[1]	+0.0011
3..........	0.3566	0.3562	—0.0004	0.2403	0.2412[2]	+0.0009

Rapid Determination of the Nickel.—Nickel may be rapidly separated from arsenic by using the well-established methods involving rotating electrodes and high current densities. Solutions similar to those employed in the 2 preceding sections were used. Results of typical determinations are to be found in Table III. The cathode in this series of experiments was a platinum dish of 125 cc. capacity. The speed of anode rotation was from 600 to 800 per minute.

TABLE III.

	Nickel taken. G.	Nickel found. G.	Difference. G.	Arsenic taken. G.	Current $N.D_{100}$. Amp.	Voltage.	Time for complete deposition. Min.
1..........	0.1783	0.1783	0.0000	0.4060	1.25	3.6	75
2..........	0.1783	0.1779	—0.0004	0.8120	1.25	3.8	60
3..........	0.3566	0.3564	—0.0002	0.4060	1.50	4.2	60
4..........	0.1783	0.1787	+0.0004	0.4060	3.75	8.6	25

Each deposit was tested in the manner previously described and was found to be free from arsenic.

Practical Test of the Method.—As a further test of the method a sample of niccolite (arsenide of nickel) was examined. The samples of the mineral were brought into solution by treatment with appropriate amounts of conc. nitric, hydrochloric, and sulfuric acids. After the excess of nitric and hydrochloric acids had been volatilized the small quantity of iron present was precipitated by the addition of ammonium hydroxide. The precipitate was freed from nickel by repeated precipitations with ammonia, after the ferric hydroxide had been dissolved in hot dil. sulfuric acid. The resulting ammoniacal solution of nickel was then electrolyzed, with the conditions as nearly as possible those described under "Test Separations." The mineral examined contained only a very small amount of cobalt. The per cent. of metal found by the electrolytic method was (1) 38.12, (2) 38.08, (3) 37.88. Previous examination of the material by Mr. F. K. Dimon, a former honors student, who used the excellent volumetric method of Moore,[1] had yielded (1) 38.10, (2) 37.74, (3) 37.97% of metal.

It is, of course, evident that copper, if present in such a mineral, will be deposited along with the nickel and cobalt. The amount of the copper may be readily determined by electrolyzing the nitric acid solution of the deposit.

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[1] Moore, *Chem. News*, **59**, 160 (1889); **72**, 92 (1895).

Summary.

Experimental results have been communicated which prove that nickel may be quantitatively separated from salts of arsenic acid in ammoniacal solution by means of the electric current.

The striking and radical difference between the behavior of cobalt and nickel when deposited from such solutions has been pointed out. This interesting property of cobalt is being made the subject of further study in order to determine why arsenic is always deposited with cobalt and not with nickel.

In conclusion the writer wishes to thank Dr. L. W. McCay for very valuable advice and suggestions during the progress of this work.

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[CONTRIBUTION OF THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY.]

A STUDY OF THE VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF MANNITE.[1]

BY J. C. W. FRAZER, B. F. LOVELACE AND T. H. ROGERS.

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Introduction.

The vapor pressure method offers certain advantages for the investigation of the colligative properties of solutions, and, though many efforts have been made to apply it to the study of aqueous solutions, the results have not been entirely successful. The fundamental importance of the knowledge of the vapor pressure of solutions is shown by its frequent use in thermodynamic formulas. In practice 2 methods, known as the dynamic and static methods, have been used. The first depends on the determination of the amount of the solvent required to saturate the same volume of air when in equilibrium with the solvent and solution, respectively, both maintained at the same constant temperature. This method has been used by Ostwald; the Earl of Berkeley[2] and his associates have investigated the various sources of error involved in this method and have made many improvements in the apparatus and details of manipulation. The recent work of Washburn[3] has been essentially an application of the apparatus of Berkeley.

Some time ago Frazer and Lovelace,[4] in spite of the failure of earlier workers, described an apparatus and manipulation by which accurate measurements of vapor pressure of aqueous solution by the static method could be made. Many of the errors which had previously been encoun-

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[1] The experimental part of this article forms the basis of a dissertation submitted by T. H. Rogers to the Johns Hopkins University.

[2] *Proc. Roy. Soc. A.*, **17**, 156 (1906).

[3] Washburn, THIS JOURNAL, **37**, 309 (1915).

[4] Frazer and Lovelace, *ibid.*, **36**, 2439 (1914); *Z. physik. Chem.*, **89**, 155 (1914).