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AN ANNOTATED BIBLIOGRAPHY OF
ANALYTICAL METHODS FOR ALKALI METALS

E. E. Garcia
B. D. LaMont

MASTER

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APPROVED:

Neil E. Gordon, Jr.
N. E. Gordon, Jr.
Technical Service Labs
Chemical Development

APPROVED:

P. Cohen
P. Cohen, Manager
Chemical Development

Westinghouse Electric Corporation
Atomic Power Division
P. O. Box 355, Pittsburgh, Pa. 15230

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1.0 INTRODUCTION

Liquid metal technology is assuming an increasingly important role in the future of the nuclear power program. In liquid metal technology, coolant purification systems such as cold traps are of extreme importance. The primary cold trap of the Enrico Fermi Reactor has experienced a variety of operating conditions with an abnormal range of contaminants, and provides a unique opportunity to extend our knowledge of cold trap performance and to help establish bases for future cold trap designs.

Westinghouse Atomic Power Division is conducting a program, under sponsorship of the U. S. Atomic Energy Commission, to evaluate the performance of the primary cold trap from the Enrico Fermi Reactor. Samples will be collected from various spacial locations within the cold trap and will be analyzed for sodium oxide, sodium hydroxide, carbon, carbonates, carbides, nitrogen compounds, and metallic impurities. As part of this work, a review of analytical methods for alkali metals has been performed and is now presented as an annotated bibliography.

More than one hundred references have been abstracted. When a paper has been published in more than one place, for example, in a periodical publication or as an AEC Report, reference is made first to the more readily available source, while all other sources are also indicated.

In a few cases, abstracts of papers related to other elements have been included, because those procedures can be adapted, or have been adapted, to alkali metal analysis.

2.0 GENERAL REFERENCES

2.1 Kallmann, S.

"The Alkali Metals" in "Treatise on Analytical Chemistry" edited by I. M. Kolthoff and P. J. Elving.
Interscience Publishers, New York, 1961, Part II, Vol. 1, p. 306.

2.2 Perrine, H. E.

"Collected Methods for the Analysis of Sodium Metal"

US AEC Report, GEAP-3273 (1959)

Procedures for the determination of several elements in sodium metal are given. Calcium is determined by EDTA titration using Calcein as indicator. Carbon is determined by wet combustion by the Pepkowitz and Porter procedure (Ref.7.1). Chromium is determined spectrophotometrically with s-diphenylcarbazide. Iron is determined spectrophotometrically with o-phenantroline. Lithium is determined by flame photometry. Nickel is determined spectrophotometrically with dimethylglyoxime. Sodium Monoxide is determined in two different ways. When the monoxide is a major constituent, the "free" sodium is determined by measuring the hydrogen evolved during methanol dissolution. Total sodium and sodium bicarbonate are determined by titration. The sodium oxide is determined by difference. When the monoxide is present as a trace constituent, mercury amalgamation is used. Potassium is determined by flame photometry. Zirconium is determined spectrophotometrically with alizarin reagent. Other impurities are determined by spectrographic techniques.

2.3 "The Analysis of Sodium Metal and NaK (Collected Capenhurst Methods)"

UKAEA Report IGO-AM/CA-110 (1958)

Carbon is determined by a wet combustion-manometric procedure. Carbonate is determined by acid decomposition, absorption of the released carbon dioxide in barium hydroxide and titration of excess barium hydroxide with acid. Oxygen is determined by an amalgamation procedure.

- 2.4 Sittig, M.
"Sodium, its Manufacture, Properties and Uses"
ACS Monograph, Reinhold, New York, 1956.
- 2.5 Jackson, C.B. (Editor)
"Liquid Metals Handbook. Sodium NaK Supplement"
Atomic Energy Commission and Bureau of Ships, US AEC Report
TID-5277 (1955)
- 2.6 "ACS Specifications, Reagent Chemicals"
American Chemical Society, Washington, D.C., 1960, p. 434.
Specification analysis for chloride, nitrogen, phosphate, sulphate,
heavy metals and iron in sodium metal.
- 2.7 Rosin, J.
"Reagent Chemicals and Standards"
Third Edition, D. Van Nostrand Co., New York, 1955, pp. 319-385.
Specification analysis for chloride, nitrogen, sulfate, heavy metals,
iron, and sodium in potassium metal, and chloride, nitrogen, phosphate,
sulfate, heavy metals and iron in sodium metal.

3.0 GENERAL SAMPLING AND DISSOLUTION TECHNIQUES

Note: Sampling and dissolution procedures are usually described in detail in the articles on individual analytical procedures.

- 3.1 Bruggeman, W.H. and Billuris, G.
"Sampling of High Temperature Alkali Metals"
US AEC Report AECU-2143 (1953)
Samples for the determination of oxygen in sodium by the Pepkowitz and Judd procedure (Ref. 5.1) were initially obtained by a vacuum thief tube technique. Results obtained by this technique were not completely satisfactory and the thief was replaced by a sampling device comprising

an inert gas-filled steel box fitted with a heated inlet line and drain line, together with a manipulator for transferring sample cups into a sample carrier which could be fitted to the analytical apparatus.

3.2 Humphreys, J.R.

"Sampling and Analysis for Impurities in Liquid Sodium Systems"

Chem. Eng. Progr. Symposium Series 53, 7 (1957)

A representative sample is drawn into a metal-foil-lined metal receiver. The sodium is removed from its impurities by vacuum distillation directly in the sampler and the residue is analyzed by either radiological or chemical methods. The method is also applicable to other liquid metal systems such as potassium, NaK, mercury, rubidium and cesium.

3.3 Chevilliard, H.

"Liquid Sodium Sampler"

Report Commissariat a l'Energie Atomique (France) CEA-834 (1959)

A sampler for liquid sodium which permits its introduction into a detachable container without atmospheric oxidation is described. During operation the pressure does not exceed 5×10^{-5} mm Hg.

3.4 Goldberg, G., Meyer, A.S. and White, J.C.

"The Sampling of Alkali Metal Systems with the Modified MSA Sampler"

US AEC Report ORNL-2147 (1956)

The original MSA sodium sampler has been modified by replacing the packing gland and the gate valve by vacuum tight components.

3.5 Kharlamov, V.T.

"Preparation of Analytical Samples of Alkali Metals for Vacuum Extraction"

Trudy Komissii Anal. Khim., Akad. Nauk SSSR 10, 117 (1960)

The method consists of cutting a measured, extruded column of alkali metal in high vacuum (10^{-4} mm Hg) by means of a heated nichrome wire operated from the outside of the apparatus. A similar method is described for NaK samples, where the alloy is poured in vacuum into a small cup of known volume. Samples obtained this way can be reproduced with differences in weight of about 1.5%.

3.6 Pepkowitz, L.P.

"Dissolving Sodium-Potassium Alloys"

Anal. Chem. 26, 574 (1954)

The NaK sample is frozen by placing it in a glass dish supported on dry ice. The container is broken, and the solid NaK piece is cut into small pieces and dropped into an alcohol-dry ice slurry. The reaction is very smooth at this temperature and can be controlled by either warming slightly or by adding dry ice. The resulting carbon dioxide blanket prevents reaction with the oxygen in the air. By this means, a 1 g. sample of NaK can be dissolved in 15 minutes.

3.7 White, J.C., Talbott, C.K., and Brady, L.J.

"Dissolution of Sodium-Potassium Alloys for Purposes of Analysis"

Anal. Chem. 26, 942 (1954)

The sample of alloy is placed in a beaker containing enough n-hexane to cover the sample completely. The beaker rests on a mineral oil bath. A funnel is inverted over the beaker and a blanket of helium or argon placed over the solution. Absolute methanol or ethanol is added drop-wise until the reaction is complete. When the reaction is complete, an excess alcohol is added, and then water to dissolve the alcoholate formed. The two phases are then transferred to a separatory funnel and the water layer is separated. This procedure has been used to dissolve samples of NaK in the range 0.05 to 25 g.

4.0 CHEMICAL METHODS FOR THE DETERMINATION OF THE UNCOMBINED ALKALI METAL

4.1 Eddy, L.B., Messner, A.E. and Weber, A.E.

"Determination of Free Sodium in Sodium Hydride"

Anal. Chem., 30, 1971 (1958)

(also, US AEC Report CCC-1024-TR-186 (1956))

Butyl bromide reacts quantitatively with sodium dissolved in liquid ammonia. Butyl bromide, dissolved in n-hexane, is added to the solution until the characteristic blue color of the sodium-ammonia complex disappears. Sodium hydride does not react with butyl bromide under these conditions. The reaction was applied to the determination of free sodium in sodium hydride-mineral oil slurries.

- 4.2 Berkenblit, M. and Reisman, A.
"Analysis of Lithium Metal and Lithium (I) Mixtures"
Anal. Chem. 32, 721 (1960)
Metallic lithium is determined in presence of lithium salts by treating the metal with water, added dropwise, in an oxygen stream. The hydrogen formed is carried by the oxygen through a series of phosphorus pentoxide drying towers and then converted to water by passing through a tube filled with platinum wool heated to 450°C. The water formed is determined gravimetrically after absorption on phosphorus pentoxide. The total lithium is determined by titrating the residue with acid.
- 4.3 Kozlov, F. A.
"Gasometric and Gravimetric Methods of Assaying Sodium for its Oxygen Content. Application to the Analysis of the Contents of Oxide Traps"
Atomnaya Energiya 12, 332 (1962)
Sodium containing oxide is analyzed by reaction with water or ethanol. The measurement of the evolved hydrogen permits the calculation of the metallic sodium content. The total sodium is determined by titration. The gravimetric method involves weighing a sample and finding its volume by immersion in mineral oil. The oxide content is calculated from the known specific gravities of sodium and sodium oxide. These procedures have been applied to the analysis of cold traps where the oxide content is 2.5 - 12%.
- 4.4 Bannykh, E.S. and Sachko, A.P.
"A Rapid Method of Inspection of Metallic Potassium for Potassium and Sodium Content"
Trudy Ural, Nauch. Issledovatel. Khim. Inst. No. 4, 209 (1957)
The method is based in separate determinations of the total alkalinity and of the solidification temperature of the potassium metal sample.

5.0 CHEMICAL METHODS FOR THE DETERMINATION OF OXYGEN

- 5.1 Pepkowitz, L.P. and Judd, W.C.
"The Determination of Sodium Monoxide in Sodium"
Anal. Chem. 22, 1283 (1950)
also, US AEC Report KAPL-P-452 (1949)

The sample is treated with mercury in a suitable apparatus under a nitrogen atmosphere until all the sodium is converted to an amalgam. Any sodium monoxide present is not amalgamated and floats on the surface. The oxide is dissolved in water and titrated with 0.005 N hydrochloric acid to a phenolphthalein end point. Samples containing 0.02 to 1% oxygen can be analyzed satisfactorily in this manner.

5.2 Pepkowitz, L.P., Judd, W.C. and Downer, R.J.

"Determination of Sodium Monoxide in Sodium, An Addendum"

Anal. Chem. 26, 246 (1954)

also, US AEC Report KAPL-972 (1953)

Two modifications to the original procedure (see ref. 5.1) resulted in an increased precision. In the first, nitrogen is freed of oxygen by bubbling through NaK instead of passing through hot copper. In the second, the mercury is warmed during the amalgamation. These modifications have improved the precision from 0.01% to 0.001% (absolute).

5.3 Williams, D.D. and Miller, R.R.

"Modified Apparatus for Determination of Sodium Monoxide in Sodium"

Anal. Chem. 23, 1865 (1951)

Description of a high vacuum, all-glass apparatus for the determination of sodium monoxide in sodium by the amalgamation technique.

5.4 Champeix, L., Darras, R. and Duflo, J.

"Oxygen Determination in Sodium The Mercury Method and its Use for Very Low Values"

J. Nuclear Materials 2, 113 (1959) (in French)

also, US AEC Report AEC-TR-5840 (English translation)

also, Report Commissariat a l'Energie Atomique (France) No. 835 (1958)

Oxygen is determined by a modification of the amalgamation method, in which the residual sodium is determined by flame photometry. The lowest concentration measured was 7 ppm with a reproducibility of ± 1.5 ppm.

It was concluded that the technique could be extended to the determination of 1 ppm of sodium if the problem of sample contamination during transfer could be solved.

- 5.5 Minczewski, J., Wasowicz, S. and Dancewicz, D.
"Determination of Oxygen in Metallic Sodium"
Chem. Anal., Warsaw, 6, 741 (1961) (in Polish)
also, Polish Academy of Sciences, Institute for Nuclear Research,
Report PAN-256/VIII (1961) (in Polish)
also, Acta. Chim. Acad. Sci. Hung. 33, 51 (1962) (in Russian)
The method is based on amalgamation of the sodium with mercury in a
simplified apparatus. The insoluble oxide is dissolved in water and
determined by flame photometry. The amalgam is hydrolyzed with 5 N
hydrochloric acid and the sodium determined by titration to determine
the sample weight. The standard deviation was about 13 ppm for 50-150
ppm of oxygen.
- 5.6 Jahns, W. and Weidmann, G.
"Determination of Low Oxygen Contents in Sodium"
Nukleonik 1, 189 (1959) (in German)
Oxygen is determined by a simplified amalgamation method.
- 5.7 Malikova, E.D. and Turovtseva, Z.M.
"Determination of Oxygen in Alkali Metals and Their Alloys by Mercury
Extraction"
Trudy Komissii Anal. Khim., Akad. Nauk SSSR, 10, 91 (1960)
The method of Pepkowitz and Judd (Ref. 5.1) was employed. The sensitivity
was 0.001% and the accuracy 10% relative.
- 5.8 Steinmetz, H. and Minushkin, B.
"Experimental Determination of Contaminants in Sodium"
US AEC Report NDA 2154-6 (1961)
Procedures for the analysis of carbon and oxide are described. Oxygen
is determined by an amalgamation procedure. After the bulk of sodium
is removed, the residue is dissolved in anhydrous methanol, an organic
acid is added and the water formed in the reaction between the oxide and
the acid is titrated with Karl Fischer Reagent. The method was applied
to samples containing 3 ppm of sodium and the standard deviation was $\pm$
1.5 ppm. Carbon is determined by a modification of the Pepkowitz and
Porter procedure (Ref. 7.1).

5.9 Stern, G.

"Analytical Method for the Determination of Oxygen in Sodium"

US AEC Report TID-7623, pg 161

The method combines mercury amalgamation and Karl Fischer titration in order to improve sensitivity and avoid sources of error. The method is useful for the measurement of oxygen in the 1-10 ppm range.

5.10 White, J.C., Ross, W.J. and Rowan, R.

"Determination of Oxygen in Sodium"

Anal. Chem. 26, 210 (1954)

also, USAEC Report ORNL-1286 (1952)

The method is based on the fact that n-butyl bromide (1-Bromobutane) reacts with sodium to form sodium bromide, but does not react with sodium oxide. An inert diluent is required to avoid an explosive reaction. Hexane is satisfactory. The sodium sample is treated with a 50% solution of n-butyl bromide in hexane. The mixture is heated at 60-70°C for 1 to 2 hours. When the reaction is complete, carbon dioxide-free water is added to dissolve the residue. The phases are separated and the aqueous phase is titrated to pH 7 with 0.001 N nitric acid using a glass electrode.

The method is satisfactory for samples of sodium containing more than 0.02% oxygen. The standard deviation is in the order of 0.003 to 0.005% (absolute). Samples as large as 20g can be handled.

5.11 Silverman, L., and Shideler, M.

"Determination of Oxygen in Sodium and in Sodium-Potassium Alloy by the Butyl Bromide Method"

Anal. Chem. 27, 1660 (1955)

also, "Experimental Techniques for the Determination of Oxygen in Sodium and in NaK by the Butyl Bromide Method"

USAEC Report NAA-SR-1509 (1956)

Modifications were suggested for the butyl bromide method of White, Ross and Rowan. The organic reagents are purified by passing through a silica gel column and dried over aluminum oxide. By this means the water content of the reagents is reduced to less than 0.5 ppm. The sample

ampule is open under n-hexane by means of special pliers. Finally, the method is adapted to analysis of oxygen in NaK alloy by initially freezing the alloy and then controlling the speed of reaction by changing the temperature of the mixture. After all the potassium has reacted, the sodium reaction is hurried by increasing the content of butyl bromide.

5.12 Smythe, L.E. and DeBruin, H.J.

"The Determination of the Oxygen Content of Sodium Metal by the Butyl Bromide Method"

Analyst 83, 242 (1958)

Potentiometric titration of the residue left after treatment of the metallic sodium with butyl bromide is subject to large error. Accurate results are obtained if a water-ethanol solution of sodium hydroxide, containing 5-8g of sodium bromide, is employed for the titration, and the end point is detected with a visual indicator.

5.13 DeBruin, H.J. and Smythe, L.E.

"Determination of Traces of Oxygen in Sodium Metal by Infrared Spectrophotometry"

Nature 182, 387 (1958)

Sodium metal, containing 5-100 ppm of oxygen, is allowed to react with an alkyl halide. Excess carbon dioxide is then passed into an aqueous solution of the reaction mixture. The solution is freeze-dried, and the residue is heated at 400°C for two hours. Thus, the sodium monoxide is converted successively to hydroxide and then to carbonate in a sodium bromide matrix. The final mixture is compressed into a disc which is analyzed by infrared spectrophotometry. The band at 11.38 microns is used. It does not obey Beer's law but standard curves of absorbance vs oxygen concentration can be drawn. Oxygen can be determined by this procedure with an accuracy of ± 10 ppm.

5.14 DeBruin, H.J.

"Determination of Traces of Oxygen in Sodium Metal by Infrared Spectrophotometry"

Anal. Chem. 32, 360 (1960)

Sodium is converted to sodium chloride by a Wurtz reaction using n-amyl chloride. Any sodium oxide present remains unchanged. The reaction products, containing the oxygen impurity, are filtered off and dried. The sodium oxide is converted to carbonate by atmospheric carbon dioxide. The reaction products are pressed into a disc and the carbonate present is measured by means of its absorbance band at 11.38 microns. This band follows Beer's law between 0-300 ppm in a sodium chloride matrix. The lower limit is 20 ppm of oxygen with an accuracy of $\pm 20\%$.

5.15 Eberle, A.R., Lerner, M.W. and Petretic, G.J.

"Determination of Oxygen in Calcium Metal"

Anal. Chem. 27, 1431 (1955)

Calcium metal is dissolved in anhydrous methanol in a flask fitted with a condenser. When the reaction is complete, a solution of salicyclic acid in pyridine is added. This solution reacts with the calcium oxide present to give calcium salicylate and water. The water formed is titrated with Karl Fischer reagent using a dead stop end point. All the reagents are pretritrated with Karl Fischer reagent. The method can be applied to samples containing 0.4 to 2.0% of oxygen with an error of less than $\pm 5\%$ relative.

5.16 Sax, N.I. and Steinmetz, H.

"Determination of Oxygen in Lithium Metal"

USAEC Report ORNL-2570 (1958)

Lithium oxide in lithium will react with methanol to produce the hydroxide which in turn reacts with salicyclic acid in pyridine to produce water. The amount of water, proportional to the oxygen present, is determined with Karl Fischer reagent.

5.17 White, J.C.

"Procedure for the Determination of Oxygen in Sodium and NaK by the Distillation Method"

USAEC Report CF-56-4-31 (1956)

The liquid metal is sampled at operating temperatures directly into the distillation apparatus, where a fixed volume is retained in a hemispherical cup. The metal is distilled from the oxide at a temperature of 800°F

and at a pressure of less than 5 microns of mercury. After the metal has been distilled, the residue in the cup is dissolved in water and titrated with hydrochloric acid using methyl orange as indicator.

5.18 Humphreys, J.R.

"Sampling and Analysis for Impurities in Liquid Sodium Systems"

Chem. Eng. Progr. Symposium Series 53, p. 27 (1957)

See Ref. 3.2

5.19 Smith, C.R.F.

"Determination of Oxygen in Sodium - A Critical Review of Analytical Methods"

USAEC Report NAA-SR-Memo-2061

Several methods of measuring the sodium oxide content of liquid sodium are reviewed. The amalgamation method shows poor reproducibility and cannot distinguish between Na_2O , NaH , Na_2CO_3 , Na_2O_2 and NaOH . The distillation method is subjected to interference from elements that can reduce sodium monoxide, but sodium hydride does not interfere. The butyl bromide method is subjected to errors from sodium carbonate, peroxide and hydroxide but probably not from hydride. The methanol-organic acid-Karl Fischer reagent method has high blanks and is extremely sensitive to traces of water in the reagents.

It is concluded that there is no proved method that can be applied to the determination of trace amounts of oxygen in sodium metal.

5.20 Jaworowski, R.J., Potts, J.R. and Hobart, E.W.

"The Determination of Oxygen in Lithium"

Anal. Chem. 35, 1275 (1963)

The alkali metal sample is dissolved in anhydrous liquid ammonia, and the oxides are separated by filtration through a fritted glass filter. The insoluble oxides are dissolved and titrated with coulometrically generated hydrogen ion. Nitrogen dissolved in lithium samples is not

retained by the filter. Titration curves show the presence of carbonate in an amount approximately equivalent to the total carbon content of the lithium. The method was also applied to other alkali metals and results obtained for samples of sodium, potassium and cesium are comparable to those obtained by the amalgamation procedure.

5.21 Goldberg, G.

"Determination of Oxides and Nitrides in Lithium Metal by High Temperature Fluorination with Potassium Bromotetrafluoride"

Anal. Chem. 34, 1343 (1962)

The $KBrF_4$ method for the determination of oxygen and nitrogen in fluoride salts and metals (Goldberg, et al., Anal. Chem. 32 314 (1960) was applied to the analysis of lithium with satisfactory reproducibility.

5.22 Turovtseva, Z.M. and Litvinova, N.F.

"Determination of Gaseous Impurities in Structural and Other Materials" Proc. Second U.N. Intern. Conf. Peaceful Uses At. Energy Geneva, 28, 593 (1958)

A vacuum fusion procedure is used for the determination of oxygen in sodium and NaK. The oxygen reacts with the graphite crucible and is released as carbon monoxide. Oxygen containing compounds, like carbonate, hydroxide and peroxide are converted to monoxide at 400°C. The sample is loaded in a graphite crucible and heated to 1200°C in a period of 10 minutes. The carbon monoxide is released in 8-9 minutes and the extraction is continued for 12 minutes.

In the determination of oxygen in NaK, a molybdenum crucible filled with graphite powder is used because graphite crucibles break on contact with NaK. A sample loading system is described. The oxygen recovery was checked by running known amounts of sodium peroxide and hydroxide. The reproducibility at the 0.0075% level was ± 0.0011 . The same sample was run by the amalgamation procedure and gave an oxygen content of 0.0056%.

- 5.23 Litvinova, N.F., Malyshev, V.I., and Turovtseva, Z.M.
"Determination of Oxygen in Sodium and in Sodium-Potassium Alloy"
Trudy Komissii Anal. Khim., Akad. Nauk SSSR, 10, 97 (1960)
An apparatus is described for the determination of oxygen in sodium by vacuum fusion. The apparatus is provided with two heating chambers so that two simultaneous analysis can be made. The method is sensitive to 0.001% and the accuracy is 15-20%.
- 5.24 Born, H.J. and Wilkniss, P.
"On the Activation Analysis of Oxygen with Help of the Reaction $O^{16}(t,n)F^{18}$ "
Intern. J. Appl. Radiation and Radioisotopes 10, 133 (1961)
The reaction $O^{16}(t,n)F^{18}$ was used for the determination of oxygen in lithium and thorium. The neutron source was a swimming pool reactor. After irradiation, the metal was dissolved in methanol and water. Glass wool, sulfuric acid and sodium fluoride were added. The F^{18} was distilled as fluosilicic acid and then precipitated as lead chlorofluoride. The activity was counted using a NaI (Tl) crystal detector.
- 5.25 Faraday, B.J. and Bingham, C.R.
"Determination of Oxygen, Carbon and Nitrogen in Lithium and Lithium Hydride by Photon-Activation Analysis"
Naval Research Laboratory, Report NRL Prog. 1962, PB181071, pg 5
Photon-activation analysis is suitable for the determination of light impurities in light elements. A simultaneous determination of oxygen and carbon, and the establishment of an upper range for nitrogen in a sample of lithium and lithium hydride can be made by the analysis of position activity produced by irradiation in the bremsstrahlung beam of the NRL betatron. The sensitivity of the method is limited only when the sample contains two or more impurities which yield position-emitting isotopes of approximately the same half-life.

- 5.26 Grieser, D.R., Cocks, G.G., Hall, E.H., Henry, W.M. and McCallum, J.
"Determination of Oxygen in Sodium at Concentrations Below 10 ppm"
USAEC Report BMI-1538 (1961)

Several approaches to the problem are critically reviewed. Empirical studies were made to determine the applicability of ellipsometry, polarography, coulometry, mass spectrometry and emission spectrography as low-level oxygen-in-sodium detection methods. Ellipsometry shows little promise of specificity, but the other four are technically feasible. However, no success was achieved with any of these methods.

6.0 MECHANICAL AND ELECTRICAL METHODS FOR THE DETERMINATION OF OXYGEN

- 6.1 Gray, I.L., Neal, R.L., and Voorhees, B.G.

"Inexpensive Way to Control Oxygen in Sodium Heat-Transfer Systems"
Nucleonics 14 (10), 34 (1956)

Two types of plugging indicators are described. One, the "batch design" consists of a closed loop of 1/4 inch piping. The flow restriction is a 1/8 inch thick plate containing eight 0.050 inch diameter holes. The other one, "bypass design", consists of an air cooler, made of nine turns of 1-inch tubing coiled on 6 inches of diameter. It has a perforated plate, 1/8 inch thick, having sixteen 0.050 inch diameter holes. A thermocouple is located near the perforated plate. Either type of indicator gives an indication of the sodium oxide content by measuring the change in flow after the device is cooled 10-20°F below the temperature of the system.

- 6.2 Hall, W.A. and Draycott, A.

"Improvements in or Relating to Apparatus for Determining the Metal Oxide Content of an Alkali Liquid Metal"

Brit. Patent 883,632, date appl. 25-4-58

The apparatus comprises two channels, each containing a barrier having orifices to permit the flow of liquid metal. The barrier is resistant to corrosion by the liquid metal, but is corroded by the liquid metal containing oxide. Connecting the two channels in parallel, the oxide concentration can be determined by comparing flow rates.

- 6.3 Billuris, G. and Voorhees, B.G.
"Monitoring System for Determining the Solute Content of Solutions"
Patent U.S. 2,997,874, August 29, 1961
The apparatus is designed to monitor the oxygen content of sodium in a cooling system and to provide oxygen removal whenever it exceeds a predetermined value.
- 6.4 Blake, L.R.
"Resistivity Monitor to Indicate Oxide Content of Sodium"
Proc. Inst. Elec. Engrs. (London), Part A, 107, 383 (1960)
The electric resistivity of sodium is measured while flowing at operational temperature to provide an indication of impurity level, particularly of oxygen. The meter is designated to be sensitive to changes of 1 ppm in oxygen level, corresponding to a change in resistivity of about one part in 10^4 . There is no contact between liquid metal and meter.
- 6.5 Blake, L.R. and Eames, A.R.
"Electrical-Resistivity Meter Monitors Oxygen Contents of Liquid Metals"
Nucleonics 19, 66 (1961)
Description and application of the electrical-resistivity meters (see Ref. 6.4).
- 6.6 Blake, L.R.
"Apparatus for Indicating the Metal Oxide Content of a Liquid Metal"
U.S. Patent 3,078,412, February 19, 1963
An apparatus for measuring small changes of electrical resistivity is designed for indicating the content of metal oxide and other impurities in a liquid metal, particularly sodium.
- 6.7 Horsley, G.W.
"Possible Galvanic Cell Method for Monitoring the Activity of Oxygen in a Hot-Trapped Sodium Coolant Circuit"
UKAEA Report AERE-R-3037 (1961)

The hypothetical cell: sodium (saturated with Na_2O) - anodic oxide electrolyte-sodium (unsaturated with Na_2O) is the basis for the monitor, which would be useful in the range of 1-10 ppm oxygen.

6.8 U.K.A.E.A.

Patent Belg. 612,411, January 31, 1962

Brit. Pat. Appl. January 9, 1961

The oxygen content of fluids is determined by measuring the e.m.f. of an electrolytic cell where the fluid itself is one electrode. The reference electrode is a liquid metal saturated with its lower oxide. The method is applicable to the measurement of oxygen in the coolants of nuclear reactors.

6.9 Steinmetz, H.

"Development of a Continuous Meter for Oxygen in Sodium"

USAEC Report UNC-5032 (1962)

An electrochemical method for monitoring sodium for its oxygen content has been shown to be feasible. The cell: $\text{M,MO/ZrO}_2 + \text{CaO/Na, Na}_2\text{O (Na)}$ was used. M and MO represent, respectively, a suitable metal and its oxide, and this combination is used as reference electrode. $\text{Na}_2\text{O (Na)}$ represents oxygen dissolved in sodium. Various reference electrodes were tested for stability and temperature coefficient. Of these, a reference electrode of copper and cuprous oxide powder proved to be the most stable. The cell worked well as an oxygen monitor in the 550-650°F range, but reaction of the zirconia with sodium at higher temperatures interfered with cell function.

7.0 CHEMICAL METHODS FOR DETERMINATION OF CARBON

7.1 Pepkowitz, L.P. and Porter, J.R.

"Determination of Elemental Carbon in Sodium"

Anal. Chem. 28, 1606 (1956)

also, USAEC Report KAPL-1444 (1955)

Sodium is dissolved in water under nitrogen in a special flask. The solution is neutralized with 5 M sulfuric acid, a 10% excess is added, and the solution is evaporated to near dryness. The vessel is connected to a manometric measuring system. Five ml of Van Slyke combustion

liquid (chromic acid in a mixture of sulfuric and phosphoric acids) are added and the carbon present is oxidized to carbon dioxide by boiling for 5 minutes. The carbon dioxide is swept into the measuring system and measured by the freeze out technique described by Pepkowitz and Moak (Anal. Chem. 26, 1022, (1954).)

The method is applicable to the determination of elemental carbon in the range of 0.01% or less. The standard deviation at the 0.01% level is ± 0.004 using a 1g sample.

7.2 Steinmetz, H. and Minushkin, B.

"Experimental Determination of Contaminants in Sodium"

USAEC Report NDA-2154-6

See ref. 5.8

7.3 Sannier, J. and Vasseur, A.

"Analysis of Traces of Carbon in Sodium"

USAEC Report AEC-TR-5839 (in English)

also, Commissariat l'Energie Atomique (France) Report DM-1203 (in French)

Carbon is determined by a wet oxidation procedure. The oxidation with Van Slyke solution is carried out under vacuum and the carbon dioxide formed is analyzed manometrically; its purity can be controlled by gas chromatography. The method permits the analysis of carbon in the order of 10 ppm.

7.4 Stoffer, K.G. and Phillips, J.H.

"Determination of Carbon in Sodium-Potassium Alloy"

Anal. Chem. 27, 773 (1955)

The method described involves ignition of a 100 mg sample in a nitrogen-oxygen atmosphere and weighing the carbon dioxide formed after absorption on Ascarite. The oxygen is purified by passing over Ascarite, Drierite, phosphorus pentoxide, hot copper oxide and Ascarite-Drierite tubes in that order. The nitrogen is purified in a similar manner. A quartz combustion tube is used. Approximately one-half of the tube is filled with copper oxide, followed by silver wire and lead oxide. This section is heated in a 700°C furnace. A sample introduction chamber is fitted

with a push rod and is used to introduce samples in the combustion chamber without atmospheric contamination. The combustion chamber is kept cold until the sample is introduced and then is heated to approximately 1000°C by means of air-gas, blast-type burners. The absorption tubes used are the straight type Drierite-Ascarite micro-absorption tubes. Sampling procedures from dynamic systems, and the transfer of the sample to the analytical equipment are described. The procedure has been used for the determination of quantities of carbon in the order of 100 µg.

7.5 Potts, J.R. and Hobart, E.W.

"The Determination of Carbon in Lithium"

USAEC Report TID-7606, pg. 120 (1960)

Carbon in lithium metal is determined by a combustion procedure. Samples of lithium, weighing as much as 0.4 g, are ignited in oxygen at 900°C. A fluxing agent, boric oxide, is used to insure complete decomposition of the lithium carbonate formed. The combustion gases are passed through hot copper oxide and the carbon dioxide measured by the changes in conductivity in a sodium hydroxide solution. Recovery of carbon from lithium carbonate was approximately 100%. Recoveries from lithium samples containing lithium carbonate were approximately 80% in the absence of boric oxide and approximately 100% when boric oxide was used. Similar recoveries were obtained with samples containing graphite. The method appears to be more reliable than the one described by Gilbert, Meyer and White (Ref. 7.7), based on the formation of acetylene.

7.6 Herrington, J.

"Determination of Microgram Amounts of Carbon in Sodium"

UKAEA Report AWRO-62/62 (1962)

Carbon is determined by combustion in oxygen under reduced pressure. The released carbon dioxide is measured in a manometric apparatus. Amounts of carbon from 5-25 µg have been determined.

- 7.7 Gilbert, T.W., Meyer, A.S. and White, J.C.

"Spectrophotometric Determination of Lithium Carbide in Metallic Lithium as the Acetylene-Silver Perchlorate Complex"

Anal. Chem. 29, 1627 (1957)

Lithium metal is sealed in a glass ampule and placed in a stainless steel pressure vessel. Water is added and the ampule broken by shaking the container. Upon completion of the hydrolysis, the resultant gases are bubbled through a silver peroxide solution. The absorbance of the silver perchlorate-acetylene complex is measured at 297 and 313 mμ. The carbon content is read from a curve prepared in a similar manner. The coefficient of variation is 3% in the range 25-2500 ppm.

Lithium nitride present in the lithium is hydrolyzed to ammonia and can be determined by introducing a gas scrubber containing a boric acid solution. The ammonia is then determined with Nessler's Reagent.

- 7.8 Eng, K.Y., Bingham, C.D., and Meyer, R.A.

"Determination of Carbon in Sodium by Isotopic Dilution Mass Spectrometry"
USAEC Report NAA-SR-7918 (1963)

Carbon is determined in a 5g sodium metal sample by mixing it with a known amount of graphite enriched in C-13, dissolving in steam saturated nitrogen, acidifying with sulfuric acid and oxidizing the carbon to carbon dioxide with Van Slyke mixture. The carbon dioxide is collected into a cold trap and transferred to a mass spectrometer where the ratio C-12 to C-13 is measured.

The method offers the advantage that errors coming from incomplete combustion or leaks in the apparatus do not affect the final result.

In the range of 50-150 μg of carbon, the precision and accuracy were in the range ± 10-25 μg.

8.0 CHEMICAL METHODS FOR THE DETERMINATION OF HYDROGEN

- 8.1 Pepkowitz, L.P. and Proud, E.R.

"Determination of Hydrogen. Universal Gasometric Micromethod"

Anal. Chem. 21, 1000 (1949)

The sample is loaded in a sealed iron capsule and heated to 700°C in a high vacuum system. Hydrogen diffuses through the walls of the capsule

and it is measured by the change of pressure in the system. Hydroxide hydrogen can also be determined if a reductant such as sodium or magnesium is added. The average error is $\pm 0.2\%$ absolute for samples containing from 2 to 100% hydrogen. In samples containing traces of hydrogen, the error is in the order of $\pm 20\%$ relative.

8.2 Mallet, M.W., Gerds, A.F., and Griffith, C.B.

"Determination of Hydrogen in Magnesium, Lithium and Magnesium-Lithium Alloys"

Anal. Chem. 25, 116 (1953)

Two methods for the determination of hydrogen are described. In the first, the sample contained in a steel capsule is heated to 800°C in an evacuated furnace. The gases evolved are passed through a cold trap to separate any water vapor, and the hydrogen content of the evolved gas is determined by means of an Orsat apparatus. About 11 hours are required for a complete extraction.

In the second procedure the sample is dissolved in a liquid tin bath under vacuum. The bath temperature was 450°C for magnesium or magnesium lithium alloys and 300°C for lithium. The hydrogen is released rapidly and the evolved gases analyzed in an Orsat apparatus.

The tin bath procedure was found to give good results for either type of sample. Lithium results were erratic when the sample was exposed to a moist atmosphere prior to the analysis.

8.3 Bergstresser, K.S. and Waterbury, G.R.

"Determination of Hydrogen in Lithium Hydride"

USAEC Report LAMS-1698 (1954)

Hydrogen is determined in lithium hydride by heating samples in a lead bath at 600°C . The hydrogen evolved by thermal decomposition is purified and converted to water by passing over copper oxide at 400°C . The water is collected and weighed. When the procedure was applied to lithium hydride the standard deviation varied between 0.12-0.42% absolute.

8.4 Simpson, O.C. and Rauh, E.G.

"Determination of Hydrogen in Sodium-Potassium Alloy"

USAEC Report CF-3748 (1956)

The procedure consists of converting the hydrogen present in the sample to hydroxyl ion, equilibrating with deuterium oxide of known concentration and measuring mass spectrometrically the dilution of deuterium by the hydrogen.

8.5 Holt, B.D.

"Determination of Hydrogen in Alkali Metals by Isotope Dilution Method"

Anal. Chem. 31, 51 (1959)

Deuterium is added to a sampling tubing containing sodium or NaK. After heating to 460°C, a mass spectrographic analysis is made of the H/D ratio. From this, the hydrogen concentration of the metal can be determined. For the analysis of NaK, a correction is necessary due to the difference in the rate of formation of sodium and potassium hydrides and deuterides.

8.6 Evans, C. and Herrington, J.

"Determination of Hydrogen in Sodium by Isotopic Dilution with Tritium"

Anal. Chem. 35, 1907 (1963)

A sodium sample is introduced in a glass boat contained in a special sample tube. After introduction of the sample, the sampling tube is sealed and a known amount of tritium-enriched hydrogen is introduced through a stop-cock. Equilibrium between the tritiated hydrogen and the hydrogen in the sample is established by heating at 420°C for 10 minutes. The gases are then introduced into a sampling apparatus, where a gas sample is obtained for counting. The gas is purified by diffusion through palladium before the specific activity is determined by Geiger counting.

9.0 PHYSICAL METHODS FOR THE DETERMINATION OF HYDROGEN

9.1 Davis, K.A.

"Detection Device for Hydrogen in Sodium"

USAEC Report NAA-SR-5732 (1962)

The apparatus extracts hydrogen from flowing sodium by allowing hydrogen to diffuse through a nickel membrane. Measurements of the rate of rise of a vacuum system outside of the nickel barrier yields quantitative results. Spectrographic analysis of the collected gas is used to verify that the gas is hydrogen. It has been possible to detect 1.4 ppm (by weight) of hydrogen in sodium.

10.0 CHEMICAL METHODS FOR THE DETERMINATION OF NITROGEN

- 10.1 Sax, N.I., Chu, N.Y., Miles, R.H., and Miles, R.W.

"Determination of Nitrogen in Lithium"

USAEC Report NDA-38 (1958)

Nitrogen, present in lithium as the nitride, is converted to ammonia by hydrolysis and then distilled in an argon stream. The ammonia is collected in 1% sulfuric acid and determined colorimetrically with Nessler's Reagent.

- 10.2 Ward, C.H., Gardner, R.D., Ashley, W.H. and Zerwehk, A.

"The Titrimetric Determination of Traces of Nitride Nitrogen in Sodium Metal"

USAEC Report LA-2892 (1963)

A modified Kjeldahl method has been applied to the determination of nitride nitrogen in sodium. The sample is dissolved in ethanol in an argon atmosphere. The solution is diluted with water and the nitrogen is distilled as ammonia. The ammonia is absorbed in a dilute boric acid solution and titrated with 0.01 N hydrochloric acid to a methyl red-bromocresol green end point. The average recovery for 31 samples containing known amounts of nitrogen in the 1-100 ppm range was 100%. The average standard deviation over the entire range was $\pm 2.5\%$ relative.

11.0 DETERMINATION OF OTHER IMPURITIES

- 11.1 Rynasiewicz, J., Sleeper, M.P. and Ryan, J.W.

"Boron in Sodium Metal, Determination of Microgram Amounts by Alcohol Extraction"

Anal. Chem. 26, 935 (1954)

also, USAEC Report AECD-3511 (1953)

The sodium sample is dissolved in water. After complete dissolution, the solution is neutralized and evaporated to

dryness. The residue is extracted with slightly acid ethyl alcohol. The alcoholic extracts are made alkaline and evaporated in the presence of a small amount of glycerol. Curcumin solution is added to the residue, followed by an oxalic-hydrochloric acid solution. The color is developed for 1 hour at 60°C. The color of the boron-curcumin complex is read at 550 m μ . The reported accuracy is $\pm 20\%$ relative and the method can be applied to samples containing 1 ppm of B or more. The average recovery is 72%.

11.2 "Analytical Method for the Absorptiometric Determination of Boron in Sodium Metal"

UKAEA Report PG-Report-415 (1963)

Sodium is dissolved in water under argon, and the resulting sodium hydroxide solution is evaporated to dryness. Boron is determined using curcumin. The rosocyanin formed is separated from the excess curcumin and dissolved in ethanol for the spectrophotometric measurement. The method is applicable to sodium metal containing 0.1 to 1 ppm boron with a precision of $\pm 20\%$ at the 0.5 ppm level.

11.3 Logie, D.

"A New Analytical Separation Technique by Using Ion-Exchange Membranes and Its Application to the Determination of Boron in Sodium Metal"

Chem. & Ind. (London) 1957, 225

If a solution of a metal salt is electrolyzed in a cell having the electrode compartments separated by a cation exchange membrane, the metal ions will pass irreversibly into the cation compartment. When sodium metal is converted to the hydroxide, boron is converted to borate, which will remain in the anionic compartment while the sodium ions will migrate to the cationic compartment.

11.4 Friedman, H.A.

"Analysis of Lithium Metal, Hydride and Hydroxide for Nickel, Copper, Silicon, Iron, Chromium, Aluminum and Hydroxide"

Anal. Chem. 32, 137 (1960)

Nickel is determined by the dimethylglyoxime-extraction method.

Copper is determined in the residue from the nickel determination by extraction of the carbamate complex with isoamyl alcohol.

Chromium is determined by the diphenylcarbazide method after precipitation using aluminum as a carrier. Silicon is determined by the molybdate procedure. Iron is determined as the o-

phenantroline complex; in some cases a precipitation, using zirconium as carrier, is required. Aluminum is determined using aluminon. Hydroxide is determined by reaction with benzoic acid in methanol and titration of the water formed with Karl Fischer reagent.

11.5 Friedman, H.A.

"Analysis of Lithium Metal, Hydride and Hydroxide IV. Photometric Determination of Copper"

USAEC Report Y-1059 (1957)

Copper (0-20 ppm) can be determined by extraction of the carbamate into isoamyl alcohol. Iron is removed prior to extraction by precipitation with ammonia. Nickel in large quantities interferes but can be separated by extraction of the nickel-dimethylglyoxime complex in chloroform.

11.6 Friedman, H.A.

"Analysis of Lithium Metal, Hydride and Hydroxide V. Determination of Iron"

USAEC Report Y-1060 (1957)

Trace quantities of iron in lithium metal, hydride and hydroxide can be determined by the o-phenantroline method. If the iron concentration is very low, preliminary concentration by carrier precipitation of the hydroxide with zirconium may be necessary.

11.7 Friedman, H.A.

"Analysis of Lithium Metal, Hydride and Hydroxide I. Colorimetric Determination of Nickel"

USAEC Report Y-973 (1957)

Nickel may be determined in impure solutions of lithium in the range of 0-10 μg by the dimethylglyoxime chloroform extraction procedure. In pure solutions the extraction is unnecessary since lithium does not interfere.

11.8 Friedman, H.A.

"Analysis of Lithium Metal, Hydride and Hydroxide III. Colorimetric Determination of Silicon"

USAEC Report Y-962 (1957)

Silicon is determined by the ammonium molybdate procedure. To obtain reproducible results, the sample has to be acidified with 4-5 drops of hydrochloric acid in excess of neutralization prior to the addition of the molybdate reagent.

11.9 Manning, D.L., Miller, W.K. and Rowan, R.

"Determination of Submicrogram Quantities of Chromium and Vanadium in Alkali Hydroxides"

Report USAEC ORNL-1396 (1952)

Small amounts of chromium and vanadium are separated from the alkali hydroxide solution by means of Dowex-1 in hydroxide form. Chromium and vanadium are absorbed from a 1M solution of the hydroxides and eluted together by 2M ammonium carbonate. The eluate is evaporated to small volume and aliquots taken for the determination of chromium with diphenylcarbazide and of vanadium by the indirect ferrous-o-phenantroline method.

11.10 Mann, C.K. and White, J.C.

"Extraction of Chromium with Trioctylphosphine Oxide from Acidic Solutions of Alkali Metals Salts and Its Determination in Situ as the Chromium-Diphenylcarbazide Complex"

Anal. Chem. 30, 989 (1958)

also, USAEC Report CF-56-10-86 (1956)

Microgram amounts of chromium can be determined in concentrated solutions of alkali metals by extraction in the sexivalent state with a 0.2 M solution of tri-n-octyl-phosphine oxide in benzene from either a chloride or sulfate solution. The chromium-diphenylcarbazide complex is then formed directly in the benzene solution by addition of an alcoholic solution of diphenylcarbazide. As chromium is extracted only in the sexivalent state, an oxidant is added. Argentic oxide was found satisfactory as an oxidant in sulfuric acid solutions. The coefficient of variation of the method was 9% for 2-10 μg of chromium.

11.11 Silverman, L. and Seitz, R L. .

"Determination of Microgram Amounts of Cobalt in Sodium Metal-2-Nitroso-1-Naphthol Spectrophotometric Method"

Anal. Chim.Acta. 20, 340 (1959)

also, "Spectrophotometric Determination of Cobalt in Sodium Metal"

USAEC Report NAA-SR-4005 (1959)

The sodium metal is reacted with water, neutralized with hydrochloric acid, and the cobalt is determined by reaction with 2-nitroso-1-naphthol. The colored complex is extracted with carbon tetrachloride and the absorbance is measured at 535 $\text{m}\mu$. As little as 0.1 ppm of cobalt can be detected in sodium metal using a 10g sample.

11.12 Florence, T.M.

"Estimation of Traces of Nickel in Sodium Metal"

Anal. Chim. Acta. 19, 548 (1958)

also, Australian Atomic Energy Commission Report AAEC/E-23

Traces of nickel in sodium are determined by complexation with cyanide. The absorbance of the complex is measured at 268 mμ. Iron and chromium interfere but are removed as the hydroxides.

11.13 Budd, M.S. and Bewick, H.A.

"Photometric Determination of Sulfide and Reducible Sulfur in Alkalies"

Anal. Chem. 24, 1536 (1952)

A procedure for the determination of sulfur and sulfides in alkali carbonates and hydroxides is described. Sulfide, and sulfur compounds reducible to sulfides with stannous chloride or aluminum, are determined photometrically by formation of methylene blue and p-aminodimethylaniline. The range is 0.2 to 100 ppm for a 3g sample. Color intensity is measured at 670 mμ.

11.14 Hegedus, A.J. and Dvorszky, M.

"The Microtitrimetric Determination of Traces of Arsenic in Tungsten, Molybdenum, and in Other Metals"

Mikrochim. Acta 1961, 169

Arsenic can be determined in a number of metals, including sodium, by a procedure based in the Marsh test. The arsenic mirror formed is dissolved in iodine chloride and hydrochloric acid, and the sample is titrated with iodate using an extraction end point.

11.15 Dutina, D.

"Determination of Microgram Quantities of Barium in Sodium"

USAEC Report KAPL-1425 (1955)

Barium is precipitated as barium chromate followed by filtration, acid dissolution and spectrophotometric determination of the chromate ion. Amounts of barium as low as 250 ppm can be determined by this method.

11.16 Rynasiewicz, J. and Polley, M.E.

"Calcium in High Purity Sodium Salts. Determination of Micro-Amounts by the Oxine-Oxalate Method"

Anal. Chem. 21, 1398 (1949)

Calcium can be determined in sodium and sodium salts by separation with 8-hydroxyquinoline, followed by an oxalate precipitation and titration with 0.01 N potassium permanganate. As little as 0.1 mg of calcium can be determined by this procedure.

11.17 Schuhknecht, W.

"Flame Photometric Determination of Small Amounts of Calcium in the Presence of Large Amounts of Sodium"

Z. Anal. Chem. 157, 338 (1957)

The sample, containing 0.1-1 mg of calcium and 1 g of sodium is acidified and diluted to volume. The flame intensity is measured at 622 μ and referred to a calibration curve made with solutions containing 1g of sodium in 100 ml and 0-100 ppm of calcium. For 0.1 mg the error is 30% and for 1 mg 3%.

11.18 Banerjee, D.K., Budke, C.C. and Miller, F.D.

"Spectrophotometric Determination of Traces of Calcium in Sodium. Visible and Ultraviolet Methods using Sodium Naphtalohydroxamate"

Anal. Chem. 33, 418 (1961)

Microgram amounts of calcium in reactor grade sodium are determined in 1-1.5 g samples. The samples are dissolved in ethyl alcohol and converted to the chloride. Calcium is precipitated with sodium naphtalohydroxamate, and the precipitate is dissolved in EDTA. The amount of the highly colored naphtalohydroxamate released is proportional to the calcium present. The absorbance is measured at 410 μ for amounts of calcium over 10 μ g. A 10-fold increase in sensitivity is obtained by reading at 339 μ .

11.19 Silverman, L.

"Determination of Small Amounts of Potassium, Calcium and Magnesium in Sodium Metal and Some Sodium Salts"

USAEC Report NAA-SR-162 (1951)

Metallic sodium is dissolved in methyl alcohol and converted to the chloride with hydrochloric acid. Other sodium salts are also converted to the chlorides by appropriate means. The sodium chloride is dissolved in enough water to form a saturated solution and then precipitated by passing dry hydrogen chloride. The residual potassium, calcium, and magnesium can then be determined by conventional methods. Calcium and magnesium can also be determined without separation.

11.20 Silverman, L. and Trego, K.

"Determination of Small Amounts of Potassium, Calcium and Magnesium in Sodium and Its Compounds"

Analyst 78, 717 (1953)

A 5-50 g sample of sodium is dissolved in ethyl or methyl alcohol. The sample is acidified with hydrochloric acid, evaporated to dryness and baked at 110-130°C for 4-12 hours. The weight of this residue gives the total sodium as sodium chloride. Water is added to the residue to form a saturated solution. This solution is cooled to 0°C, and saturated with dry hydrogen chloride. The supernatant solution is filtered through a porous glass filter. Potassium (as perchlorate), calcium (as oxalate) and magnesium (as oxinate) are determined in the filtrate. Good results are reported in samples containing 3-8 mg of potassium, 0.1-0.4 mg of calcium and 0.4 of magnesium.

11.21 Sadek, F. S. and Reilley, C.N.

"Determination of Ammonium and Potassium Ions in Mixtures of Alkali Metals. Use of Mercury (II) (Ethylenedinitride) Tetraacetic Acid"

Anal. Chem. 31, 494 (1959)

Ammonium ion can be determined in mixtures of alkali metals by reaction with the mercury (II)-EDTA complex. The acid liberated is proportional to the amount of ammonium ion present. The procedure is selective for ammonium ion in the presence of free ammonia and alkali metal ions.

Ammonium and potassium ions can be determined together by precipitation of their tetraphenylborate salts, dissolution in N, N'-dimethylformamide, treatment with excess mercury (II) EDTA, and back titration of the liberated EDTA with standard magnesium solution. These procedures can be applied to ammonium and potassium in the range 0.5-20 mg with an error of approximately 1% relative.

11.22 Inman, W.R., Rogers, R.A. and Fournier, J.A.

"Determination of Sodium and Potassium in Lithium Metal by Flame Photometer"

Anal. Chem. 23, 482 (1951)

Sodium and potassium are the principal impurities normally found in lithium metal. By utilizing flame photometric procedures, it is possible to determine as little as 10 ppm of both sodium and potassium without previous separation.

The small negative error due to the presence of lithium can be corrected by the use of calibration curves. The procedure yields results accurate to 10% of the amount present.

11.23 Neeb, K.H. and Bebauhr, W.

"Flame Photometric Determination of Small Amounts of Potassium in Sodium and Its compounds after Enrichment with Ammonium Tetraphenyl-Borate"

Z. Anal. Chem. 162, 167 (1958)

To determine 1-10 ppm of potassium in sodium by flame photometry, potassium must be separated from the bulk of the sodium. Sodium metal is dissolved in methanol, neutralized with hydrochloric acid and the methanol removed by evaporation. To the sodium chloride residue, 500 μ g of ammonium ion are added and potassium and ammonium are precipitated with tetraphenylboron reagent. The precipitate is dissolved in a mixture of tetrahydrofuran-water, and potassium is determined by flame photometry. At the 1 ppm level the error is $\pm$ 5%. A blank is carried through the procedure.

11.24 Angot, G.

"Separation and Determination of Traces of Sodium Contained in Potassium Salts"

Mikrochim.Acta 1959, 346

Traces of sodium can be separated from large amounts of potassium salts by absorption on Amberlite IR-120. The column is eluted with 0.5 N hydrochloric acid and sodium is finally determined by flame photometry. A lower limit of 0.001% sodium can be determined with a precision of $\pm$ 10%.

- 11.25 Polvektov, N.S. and Nikonova, M.P.

"Flame Photometric Determination of Alkali Metals in Cesium Salts"

Zavodskaya Lab. 24, 528 (1958)

Cesium, in concentrations up to 25 mg/ml, did not influence the intensity of the lithium emission in an air-acetylene flame. In the presence of 50 mg/ml of cesium, the intensity was lowered by 15%. The intensity of the sodium emission was slightly enhanced by cesium. In the case of potassium and rubidium, there was strongly marked enhancement and the calibration must be done using solutions containing cesium chloride.

- 11.26 Korenman, I M., Sheyanov, F R., Tumanov , A.A., Glazunova, Z.I. and Demin, O.I.

"Radiometric Determination of Potassium in Sodium Metal, A Ternary Alloy and Electrolytes"

Trudy Khim. i Khim. Tekhnol. 1959, 94.

A sample, 0.5-0.8 g, is dissolved in methanol. The solution is neutralized with hydrochloric acid and diluted to volume. An aliquot is acidified with acetic acid. Potassium cobaltinitrite is precipitated using a cobalt salt containing Co-60. The precipitate is separated, washed and dissolved in nitric acid and an aliquot of the solution is used to determine the cobalt content radiometrically.

- 11.27 Stepin, B.D., and Plyushev, V.E.

"Flame-Photometric Determination of Traces of Potassium in Rubidium Chloride"

Zhur. Anal. Khim. 15, 556 (1960)

Traces of potassium can be determined in rubidium chloride by a flame photometric procedure using an internal standard. The determination is run in a spectrograph with a photoelectric attachment.

11.28 Farquhar, M.C. and Hill, J.A.

"Analysis of Cesium and Rubidium Salts and Metals"

Anal. Chem. 34, 222 (1962)

Samples of cesium and rubidium metal are dissolved by placing the sample, contained in a glass ampule, under petroleum ether and adding n-butyl alcohol or ethyl alcohol in small amounts. The solution is acidified with hydrochloric acid and the organics volatilized in a steam bath. Cesium or rubidium salts are dissolved in water. Alkali metal impurities are determined by flame photometry. The emission intensity if the other alkali metals is severely enhanced, by factors of four to five, by the major component. This problem is overcome by using standards containing the same amounts of the major component. The determination of minor components is accurate to within 2.8% of the amount present, at the 95% confidence level.

11.29 Smales, A.A.

"The Determination of Trace Impurities in Liquid Metal Coolants by Radioactivation Methods"

Proc., First U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 2, 273 (1955)

Five-gram samples of NaK were irradiated for 14 days in the Harwell pile. Samples were cooled for one week and dissolved in methyl alcohol. Radio-chemical and ion exchange separations were applied. The following elements were determined by their radioactivity: mercury, chromium, rubidium, cesium, silver, antimony, strontium and cobalt.

Procedures for each element are described in an appendix.

11.30 Cabell, M.J. and Thomas, A.

"Determination of Rubidium and Cesium in Sodium-Potassium Alloys and Related Materials by Radioactivation"

UKAEA Report AERE C/R 1725 (1955)

The method is a modification of the procedure of Smales and Salmon (Analyst 80, 37 (1955)). Samples, sealed in quartz containers, are irradiated along with cesium and rubidium chloride standards. After one week of cooling, the samples are dissolved in water, carriers are added, and potassium, rubidium, and cesium are precipitated as cobaltinitrites. The precipitate is dissolved in 7.5 N nitric acid and the solution passed through a column of Zeocarb 315. Potassium is eluted with 0.1 N hydrochloric acid. Rubidium and cesium are eluted with 1 N hydrochloric acid, rubidium being eluted first. Both rubidium and cesium fractions are further purified by precipitation as cobaltinitrite, dissolution in 7.5 N nitric acid and reprecipitation as chloroplatinates in water-alcohol medium. The precipitates are filtered, dried and counted using an end-window Geiger counter.

11.31 Smales, A.A. and Loveridge, B.A.

"Determination of Submicrogram Quantities of Sodium in Lithium Metal by Radioactivation"

Anal. Chim. Acta 13, 566 (1955)

A 50-100 mg lithium sample is irradiated for 15 hours in a neutron flux of 2×10^{12} thermal neutrons/cm²/sec. Sodium standards are carried through the same procedure. After 2-3 hours of cooling, the samples are treated with ethyl alcohol saturated with dry hydrogen chloride. The insoluble sodium chloride is dissolved, purified and transferred to a counting tray. The beta activity is counted and compared to that of known standards carried through the same procedure. The method can be used for the determination of sodium in lithium from

0.02 to 300,000 ppm without any alteration of the method (except for reducing the irradiation time at the higher sodium levels).

11.32 Owen, L. E. and Ellenburg, J.Y.

"Spectrochemical Analysis of Lithium"

Anal. Chem 23, 1823 (1951)

also, Ellenburg, J.Y., Owens, L.E. and Calkins, V.P.

"The Spectrochemical Analysis of Lithium Metal"

USAEC Report NEPA-1513 (1953)

Lithium metal was analyzed for Be, Cr, Co, Fe, Ni, Nb, Mn, Mo, Ta, Ti, U, V, W, and Zr; most of these were determined in the 0.001-0.1% range. A scheme utilizing the porous cup electrode was devised using platinum as internal standard. The samples are received in either stainless steel or Armco iron capsules. These are opened by special techniques. Ethyl alcohol or water are used to dissolve the lithium. The analytical elements, either in finely divided state or as the hydroxydes, are filtered on 15 mm filter paper discs. Be, Cr, Ni, Fe, Nb and Mn have appreciable solubility in lithium hydroxide and require additional separation either as sulfides or 8-quinolates. The filter paper discs are wet-ashed and made to a sample volume of 10 ml. Platinum is added as an internal standard. The spectrographic determination is made by the porous cup technique using a DC spark. A rapid procedure for beryllium, without separation, can also be used.

Tantalum and tungsten are not found in sufficient concentration to respond to the porous cup technique. In this case, the filter paper disc is ignited, the ash mixed with copper oxide and graphite and arced in a cratered electrode.

- 11.33 Notkina, M.A. and Solodovnik, S.M.

"Spectrum Analysis Method for the Determination of Impurities in Lithium, Strontium and Barium"

Zavodskaya Lab. 23, 569 (1957)

A rapid method for the determination of impurities in lithium, strontium and barium without separation involves a conversion of the metals to carbonates by dissolution in water, precipitation with carbon dioxide and drying at 105-110°C, and direct use of the carbonates for analysis. The spectra are obtained with the d.c. arc using vertical electrodes. The carbonates are mixed with graphite and sulfur.

- 11.34 Notkina, M.A. and Solodovnik, S.M.

"Spectrographic Determination of Impurities in Alkali and Alkaline Earth Metals"

Fiz. Sbornik L'vov. Univ. 4, 341 (1958)

Spectrographic methods are described for the determination of Al, Fe, Si, Mg, Mn and Cu in lithium metal. Lithium is transformed to carbonate, mixed with graphite and excited by either an a.c. or d.c. arc. The reproductibility is 10-12%.

- 11.35 Goodfellow, G.I., Wilson, A.L., Boyd, T.H., Lloyd, L. and Serin, P.A.

"The Determination of Trace Elements in Metallic Sodium, Sodium-Potassium Alloy by the Porous-Cup Technique"

UKAEA, Industrial Group, Report SCS-R-329 (1959)

Al, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Si, Sn, Ti, V, and Zr are determined in sodium or NaK by using the porous-cup technique. Palladium is used as an internal standard. The samples are dissolved in ethyl alcohol and converted to the chloride prior to the determination.

- 11.36 Borovik-Romanova, T.F. and Farafonov, M. I.

"Application of an A.C. Arc to the Determination of Small Amounts of Sodium Potassium and Lithium in Metallic Rubidium and Cesium"

Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR, 12, 322 (1960)

The metal is converted to the chloride and loaded in the electrode, which is in the form of a cup of 20 mm diameter. Spectra are excited by means of an a.c. arc. The standards are made in cesium chloride or rubidium chloride. The concentration ranges are 0.001-1% for sodium and potassium and 0.0001-0.01% for lithium and the error is approximately $\pm 6\%$.

- 11.37 Vinogradov, A.V., Dronova, M.I., and Korovin, Yu.I.

"Chemical-Spectrographic Method for the Determination of Impurities in Alkaline Metals"

Zhur. Anal. Khim. 18, 29 (1963)

A method was developed for the determination of impurities in alkali metals. The impurities are concentrated by extraction of the 8-hydroxy-quinolates and cupferrates from aqueous solution at controlled pH. The spectrographic analysis is carried out by spark excitation using internal standard.

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