FABRICATION AND INVESTIGATION OF NICKEL-ALKALINE CELLS. PART II. ANALYSIS OF ETHANOLIC METAL NITRATE SOLUTIONS USED IN FABRICATION OF NICHEL HYDROXIDE ELECTRODES

David F. Pickett

Air Force Aero Propulsion Laboratory
Wright-Patterson Air Force Base, Ohio

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FABRICATION AND INVESTIGATION OF NICKEL-ALKALINE CELLS
Part II
Analysis of Ethanolic Metal Nitrate Solutions used in Fabrication of Nickel Hydroxide Electrodes

ENERGY CONVERSION BRANCH
AEROSPACE POWER DIVISION

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This report contains results of an effort to develop analytical techniques for an electrochemical fabrication process for nickel-hydroxide electrodes. The work was performed in the Aerospace Power Division (POE-1) of the Air Force Aero Propulsion Laboratory, Wright-Patterson AFB, Ohio under Project 3145, Task 314522, and Work Units 31452240 and 31452245. The effort was conducted by Dr. David F. Pickett during the period June 1972 to January 1975. Mr. James W. Logsdon and Mr. John Leonard collected most of the data presented. Mr. Unie D. Martin was responsible for pilot plant operation during electrode fabrication.

This report has been reviewed by the Information Office (ASD/OIP) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations. It is being given as a paper at the 147th meeting of the Electrochemical Society in Toronto, Canada.

This technical report has been reviewed and is approved for publication.

DAVID F. PICKETT
Project Engineer

FOR THE COMMANDER

DONALD P. MORTEL
Technical Area Manager

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Ethanol solutions containing nickel and cobalt nitrates are used in a recently developed process for electrodepositionof nickel and cobalt hydroxides inside nickel sinters (D.F. Pickett, U.S. Patent 3,827,911 (1974)). Nickel hydroxide electrodes, resulting from this tecnnique, have demonstrated superior performance over electrodes commonly used in aerospace Ni-Cd batteries (V. J. Puglisi, H. N. Seiger, and D. F. Pickett, Proceedings of the 9th IECEC Conference San Francisco, CA, Aug 1974, pp. 873-879). In order to control quality of

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these new electrodes several methods of analysis for impregnating solutions have been developed. These methods employ use of techniques such as gas chromatography, atomic absorption spectrophotometry, and visual spectrophotometry for individual component analysis.

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INTRODUCTION

The most widely used means of fabrication for nickel-hydroxide electrodes, such as those used in nickel-cadmium cells, is to impregnate a sintered nickel structure with active nickel and cobalt hydroxides. The methods of loading hydroxides into the sintered material, called a plaque, are varied but the most popular technique is as follows (1):

a. Dip plaque in nitrate solutions

b. Apply vacuum

c. Release Vacuum and drain nitrate solution

d. Immerse plaque in caustic solution

e. Apply cathodic current to plaque

f. Repeat steps d. through e. four to ten times

g. Apply anodic current to charge plate

This process is rather time consuming requiring several hours to prepare a finished electrode.

In Part I of this series (2), new electrochemical methods of plaque impregnation were reported that are capable of producing electrodes in a much shorter time period. These plates have been evaluated by aerospace companies (3,4,5) and show superior performance over electrodes manufactured by conventional vacuum-immersion techniques. The feasibility of industrial scale up of new electrode fabrication processes has been demonstrated partially at Spectrolab(6), Tyco Laboratories(7), and Eagle-Picher Industries(8). The work at Tyco and Eagle-Picher has been mainly sponsored by Western Electric and Bell Telephone Laboratories. The work at Spectrolab was sponsored by the Air Force Aero-Propulsion Laboratory (AFAPL). It is the purpose of the present paper to report progress on analysis methods used in controlling the Air Force process and its product.

The AFAPL process uses boiling ethanol-water solutions as a solvent medium for electrolysis of nitrate solutions. The plaque is impregnated by cathodic deposition of hydroxide from nitrate solutions of current densities of 0.3 to 0.5 amperes per square inch of plaque. Nickel counter electrodes are used. Details of the technique are given in earlier publications (2,6,9,10).

In principal, deposition of hydroxide inside the plaque occurs as a result of a decline in acidity (or increase in alkalinity) from reduction of nitrate.

A generalized equation for the cathodic half-reaction is:

$$NO_3^- + n\,H^+ + (n-1)e^- = (NO,\ NO_2,\ NH_3,\ \text{etc.}) + m\,H_2O$$

Possible concurrent half-reactions at the anode are:

$$Ni = Ni^{++} + 2e^-$$

$$CH_3CH_2OH = CH_3CHO + 2H^+ + 2e^-$$

$$CH_3CH_2OH + H_2O = CH_3COOH + 4H^+ + 4e^-$$

$$2CH_3CH_2OH + H_2O = CH_3COOCH_2CH + 3H^+ = 3e^-$$

$$2H_2O = O_2 + 4H^+ + 4e^-$$

At boiling temperatures (80°C - 83°C), the ethanol oxidation products are quite volatile. Oxidation of the anode replenishes nickel removed from solution.

From a casual observation it would appear that impurities would not present a problem in this process. The problems that arise in controlling the deposition appear mainly to arise from denaturants in the alcohol. The use of undenatured alcohol would require government controls. In applying the technique for fabrication of satellite battery electrodes, Seiger and Puglisi found that isopropyl alcohol denaturant inhibited deposition (11).

In addition to controlling undesirable components in the bath it is also necessary to maintain the level of performance enhancing additives, such as cobalt (12,13,14,15) in the electrodes. To accomplish this, cobalt levels in the bath and finished plate should be monitored. In order to initiate such controls various methods of cobalt analysis have been studied and gas chromatographic analysis of ethanolic nitrate solutions have been devised as part of the in-house development of this process. These studies and analysis methods are the subject of this report.

Experimental

Cobalt and Nickel Analysis: Three methods for determination of Cobalt presence of nickel were used: atomic absorption (16), spectrophotometric using ammonium thiocynate following extraction with ether-amyl alcohol solutions (17), titration with ethylenediaminetetraacetic acid (EDTA) followed by extraction of cobalt with 1-nitroso-2naphathol in chloroform (18). Following the chloroform extraction a second titration with EDTA is performed and cobalt is determined by difference.

Nickel was always determined using an EDTA titration. Both cobalt and nickel are titrated, and nickel is determined by difference after cobalt has been determined.

Atomic Absorption: All atomic absorption (AA) measurements were made using a Beckman Model 495 atomic absorption spectrophotometer. Single pass optics were used. Measurements for cobalt were made at wavelength 240.7 nm.

A series of Ni-Co standards were made for use in the atomic absorption spectrophotometer using 99.9% nickel foil and 99.8% cobalt power. Purity of cobalt was determined by EDTA titration. Samples were weighed to make 100 ml each of solutions with the following molalities: 1.800 Ni/0.2000 Co, 1/850 Ni/0.1500 Co, 1.900 Ni/0.1000 Co, 1.950 Ni/0.0500 Co, 2.000 Ni/0.0 Co. After dissolving in nitric acid, the sample was boiled down to a volume of approximately 25 ml. After cooling, solution was transferred to a 100 ml volumetric flask and diluted to the mark with ethanol-water solution. A 1000:1 dilution of this solution was used for running through the AA.

At least two standards were used with each sample analyzed, with concentrations above and below the sample.

Absorbance values and a Beer's Law relationship were used to determine sample concentrations.

Impregnating solutions were analyzed after filtration and 1000:1 dilution.

Electrodes were analyzed after dissolving in 7.5 molar nitric acid and dilution to 20 ppm concentration range.

Spectrophotometric: Cobalt forms a complex with ammonium thiocyanate which can be extracted with amyl alcohol-ether mixtures giving a blue solution which absorbs in the 635-640 nm range (19). Cobalt analysis of electrodes and impregnating solutions were made from an analytical procedure developed by Young (17) in which this principal was employed.

1-Nitroso-2-Naphthol Method (18): This method involves determination of combined nickel and cobalt content of a sample by addition of excess EDTA and the titration of excess with zinc, using Eriochrome Black T as the indicator. This is done with one portion of the sample solution. Using a second portion, cobalt and nickel are separated by means of a 1-nitroso-2-naphthol precipitation, followed by a chloroform extraction of the cobalt complex. The nickel content of the aqueous layer is determined by titration of an excess of EDTA and a back-titration with zinc using Eriochrome Black T as indicator. The difference between these two determinations represents the cobalt content.

X-Ray Fluorescence: X-ray fluorescence determinations of cobalt and nickel content of electrodes were made using a Phillips PW1212 X-ray Fluorescence spectrometer. Dr. Bobby L. Barnett of Michigan State University performed the analysis (22).

Analysis of Volatile Components in Imporegnating Solutions: Impregnating solutions used in nickel electrode fabrication were analyzed for volatile components using gas chromatography. Two techniques were used to remove nitrate solids from solution prior to introduction of the sample on the Poropak Q column, a distillation technique and a dual column technique. Prior to use of either technique, a column calibration procedure was employed.

Calibration Procedure: Satisfactory quantitative results may not always be obtained in gas chromatography by relating per cent area of the chromatogram to mole percent or weight per cent (20,21). In order to obtain reliable data one must calibrate the instrument for the particular components he wishes to analyze. The data given below is a result of such a calibration (singe column) for a GC-55 Beckman Gas Chromatograph using a 1/8" X 6' Poropak Q column. Conditions for calibration were:

Flow rate = 20 cc/min.

Temperature Profile = 70°C for 40 minutes then increase at a rate of 2.5 cc/min. to 190°C, then hold for 30 minutes.

Carrier Gas = Helium

A standard was prepared for components likely to be found in ethanol solutions used for impregnating sintered nickel plaques with nickel hydroxide. 1.0 µl of sample was passed thru the chromatograph under the above conditions. Results of calibration are given in Table 1 below.

TABLE 1

Calibration Data for Poropak Q Column

Component	Wt. %	Mole. %	Area %	$\frac{\text{Wt \%}}{\text{Area \%}} = f$	$\Delta f \approx \frac{W}{A^2} \Delta A$	$\Delta(W-A)^{\blacklozenge}$	Elution Time (min.)
Water	45.97	71.60	53.84±.93	0.8538	0.0003	-8.63	2.58
Methanol	2.77	2.41	2.98±.21	0.9295	0.0220	-0.21	10.14
Acetaldehyde	1.46	0.93	1.39±.09	1.0504	0.0489	-0.07	18.64
Ethanol	32.63	19.87	30.29±.62	1.0773	0.0007	2.34	37.89
Acetone	2.96	0.93	1.68±.13	1.7619	0.0811	1.28	60.50
2-Proanol	5.42	1.63	3.18±.07	1.7044	0.0118	2.24	62.25
Acetic Acid	3.64	0.98	2.10±.12	1.7333	0.0471	1.54	64.44
Ethyl acetate	5.17	1.66	4.50±.13	1.1489	0.0074	0.67	76.53

* A = area %, W = Wt.%, $A = \sum_{0}^{n} (\bar{A} - A_n)^2 / n$, $\bar{A}$ = Avg. Area

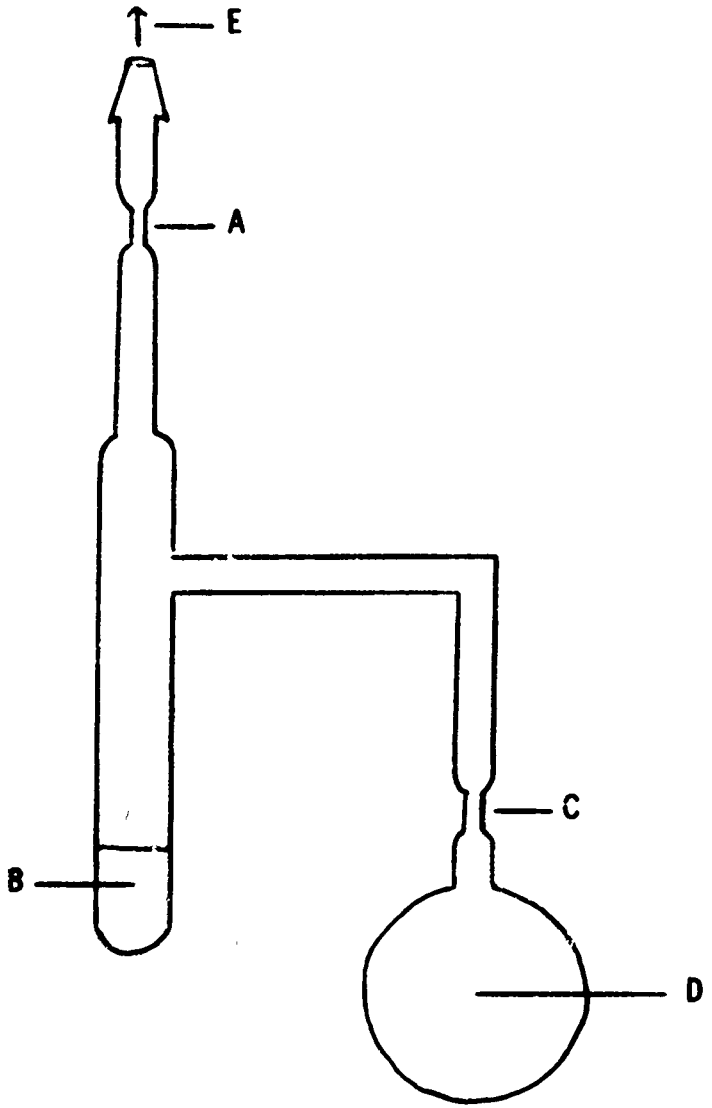
♦ (W - A) = difference between Wt % and Area %.

The above data was employed when the distillation technique, which is outlined below was used.

Distillation Technique: One technique used to separate volatiles from nickel and cobalt salts was precipitation with dimethylgloxime followed by distillation, at room temperature, under vacuum. The distilled sample is then analyzed in the gas chromatograph using the above data. In performing the distillation the apparatus shown in Figure 1 was used. The sample, about one ml, was placed in the test tube section, B, and 300 to 500 mg of dimethylgloxime added. Section B was immersed in a liquid nitrogen bath while the apparatus was evacuated. After evacuation, the apparatus was sealed at point A with a torch then allowed to thaw to room temperature. A liquid nitrogen bath was placed around D causing volatiles in B to distill over into the flask section. The flask was then sealed at point C. After warming to room temperature, the flask stem was broken and a sample taken for analysis.

Dual Column Technique: A common practice in removing solids from a liquid sample prior to gas chromatographic analysis is to pack a column with firebrick or some other absorbing solid and place this column first in series with the column used for separation of volatiles. In determinations used here, 36" of 1/8" stainless steel column containing C22 firebrick 60/80 mesh was connected prior to the poropak Q column. Conditions used were: 100°C initial temperature and flow rate of 15 cc/min for 40 minutes followed by 2.5°C/min temperature increase to 190°C then hold for 30 minutes to one hour at this temperature. Comparison of area percent to weight percent for this technique is shown in Table 2. This technique used only for determination of water and ethanol content is sometimes evidence of nitrate decomposition products were seen in the chromatogram.

Analysis of Other Components: Analysis of electrodes for carbonate and nitrate are being made on electrodes using mostly standard techniques. Carbonate is being determined using gas chromatography (23), a gas volumetric technique (24),



A. SEALABLE CAPILLARY
B. SAMPLE
C. SEALABLE CAPILLARY
D. FLASK FOR VOLATILES
E. TO VACUUM

FIGURE 1 FLASK FOR COLLECTION OF VOLATILES

and titrimetric techniques (25). At present results are incomplete and not reported. Nitrate analysis is being performed using the Kjeldahl method and selective ion electrodes.

TABLE 2
Calibration Data for Dual Firebrick and Poropak Q Column

Component	Wt. % (total)	Wt. % (vola.)	Mole % (vola.)	Area %	(W-A) %	Wt. % Area %	Retention Time (min)
Water	32.32	46.01	71.17	42.23	3.78	1.090	2.17
Methanol	3.28	4.67	4.06	7.67	-3.00	0.609	4.67
Acetaldehyde	0.89	1.06	0.33	0.28	0.78	3.786	7.42
Ethanol	31.70	45.13	22.80	45.31	-0.18	0.996	13.33
2-Propanol	0.62	0.89	0.41	0.28	0.61	1.459	63.75
Acetic Acid	0.89	1.27	0.59	0.56	0.71	1.789	67.58
Ethyl Acetate	0.74	1.06	0.33	0.28	0.78	3.786	72.42
Nickel Nitrate	26.64	-	-	-	-	-	-
Cobalt Nitrate	3.13	-	-	-	-	-	-

Data and Results

Cobalt Analysis: Of the three methods used for cobalt analysis atomic absorption was by far the most attractive. Mainly, because of ease of analysis, precision and accuracy. There are advantages to using the other methods in some circunstances. In order to obtain a relative measure of the advantages and disadvantages of these techniques a series of known nickel and cobalt solid mixtures were prepared and given to a trained technician for analysis. Results are given below. Time for the atomic absorption (AA)

TABLE 3

Comparison of Cobalt Analyses

Sample Nr	Co/Ni Ratio	Total M^{++} (by EDTA)	Co(AA)	Co (Spectro-Photometric)	Co (1-nitroso-2-naphthol)
1	0.00/1.00	1.005±.005	0.000±.001	0.000±.001	0.010±.020
2	0.030/0.97	1.004±.006	0.0299±.001	0.0296±.0020	0.0372±.0055
3	0.050/0.95	1.004±.006	0.0508±.001	0.0484±.0056	0.0565±.0067
4	0.070/0.93	1.002±.007	0.0708±.002	0.0690±.0035	0.0737±.0058
5	0.100/0.90	1.007±.009	0.1010±.001	0.0960±.0070	0.0972±.0030

analysis required from one and one-half to two hours initially plus twenty minutes for each additional sample. About six to eight hours were required for the spectrophotometric analysis, after preparation of standard solutions. An hour is required for each additional sample. Analysis time for the 1-nitroso-2-naphthol method required three to three and one-half manhours with a half hour for each additional sample.

Clearly, AA appears to give the most accurate results of the three methods, and time for analysis is markedly short. The spectrophotometric method is reliable but requires more reagent preparation. The 1-nitroso-2-naphthol extraction does not appear to be very reliable at low cobalt concentrations, but appears attractive for analysis of one or two samples with a reasonably large cobalt content. Initial equipment costs for the spectrophotometric and extraction methods are low in comparison to the AA method.

About one gram of sample was taken for each of the above analyses with dilution to one liter. Further dilution was necessary in order to use the AA and spectrophotometric methods.

Application of Atomic Absorption Analysis: The most frequent use of AA was for monitoring cobalt concentration of impregnating solutions. Electrodes were analyzed periodically for cobalt content in the total electrode and the active material. Extraction of cobalt and nickel hydroxide from the sinter was performed using methods reported by Malpert, et al., (23). Results of a typical analysis are given below:

% Co in Total Plate	% Co in Active Matl.	$Ni(OH)_2/Co(OH)_2$ Ratio	% Plate Wt. Active Matl.
3.37	8.01	6.92	42.05

Results are in reasonable agreement with X-ray fluorescence data (22).

Volatile Component Analysis: Data in Table 2 indicates that the dual column technique gives a reasonable separation of various components present in impregnating solutions, but accuracy is questionable as small peaks appear in the chromatogram superimposed on the major peaks. Apparently, these are from nitrate decomposition products. Higher than usual values for acetaldehyde acetic acid and ethyl acetate suggest that oxidation of ethanol by nitrates may be occurring. The method is reasonably suitable for ethanol and water analyses.

Table 4 shows accuracy of the distillation technique. The method is more time consuming but gives reasonable values for all components usually present.

Typical examples of component levels to be expected before and after an impregnation have been given in an earlier report (6). Ranges of denaturant impurities usually are: CH_3OH - 2-6%, $C_2H_5\ COOCH_3$ - 2-5%, unidentified components - <1%. After impregnation results are: CH_3OH - 2-6%, $C_2H_5\ COOCH_3$ - 2-6%, CH_3COOH - 0.1-1%, unidentified components -<1%. These levels do not deviate greatly after over 30 depositions.

TABLE 4

Accuracy of Distillation Technique

Component	Wt. % (volatile)	Mole. % (Volatile)	Area* %	Wt. % Using f	Δ(Wf-W)** %	% Error (Distilled)
Water	46.01	71.17	53.52±3.44	45.70	-0.31	-4.57
Methanol	5.67	4.06	4.90± .25	4.55	-0.12	-2.57
Acetaldehyde	0.97	0.61	1.24± .07	1.30	0.33	34.02
Ethanol	45.13	22.80	41.10±5.52	44.39	0-0.74	-1.64
2-Propanol	0.89	0.41	0.66± .05	1.13	0.24	26.97
Ethyl Acetate	1.06	0.31	1.11± .06	1.26	0.05	4.72

* % Area from chromatogram.

** Difference between wt.% using f and true wt.%.

DISCUSSION

Methods of analysis presented here are not entirely unique but some novel problems have arisen with respect to analysis of nitrate salts in alcohol media. Related problems are discussed in studies of analysis of NO_x-air mixtures (26,27) for control of vehicular exhaust emissions. The main problems one encounters with this type of analysis are: (1) irreversible adsorption of NO and NO_2 on column packing, (2) interaction of H_2O with NO_2, NO and O_2, (3) air oxidation of NO on the column.

In analysis of ethanol-metal nitrate solutions with gas chromatography, decomposition of nitrate on the column to give NO_2 seems to be the main concern. The distillation technique appears to eliminate this, but account of free nitric acid in solution and nitric acid formed as a result of nickel coordination with dimethylgloxime has not been made. It was not identified as an elution product. Results with this technique are very satisfactory for its application.

Cobalt analyses are straightforward, and have been discussed in the literature. Puglisi has tried a novel method using a Brinkman Probe Colorimeter (28). This method appears ideal for determining cobalt levels in impregnating solutions.

Other methods of analysis for electrodes are continuing and will be given in subsequent reports. The ones presented here are adequate for controlling pilot operations involving in-house nickel hydroxide electrode fabrication.

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