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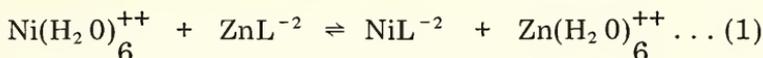
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# USE OF METAL-CHELATE DISPLACEMENT REACTION IN THE COLORIMETRIC ANALYSIS OF NICKEL

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Much work has been done on the determination of the structure and stability constants of metal chelates<sup>1</sup>, but no attempt seems to have been made for the application of metal-chelate displacement reactions to chemical analysis. It has been shown, however, that out of two metals which form similar chelates the one which has a much higher stability constant will displace the other from its chelate. Since the chelate stability constants for nickel salt and zinc salt of ethylenediaminetetraacetate differ by at least two orders of magnitude<sup>1</sup>, it was felt that the following reaction may be used for the determination of traces of nickel:



where  $\text{L}^{-4}$  represents the ethylenediaminetetraacetate ion. If the zinc ion, displaced from its chelate by an unknown amount of nickel, can be estimated precisely it will give a measure of the nickel present initially in the sample. Menon<sup>2,3</sup> has already demonstrated the use of other organic reactions for the analysis of trace elements. Although there are several spectrophotometric methods available in the literature for the analysis of nickel they suffer either from lack of sensitivity or the interference from foreign elements in the sample. On the other hand, the extraction of zinc by a solution of dithizone in carbon tetrachloride as zinc dithizonate (a red-colored species) and subsequent measurement of its absorbance have been proved to be very sensitive for the determination of zinc<sup>4</sup>. In this work attempt was made to make use of the nickel-zinc chelate displacement reaction for the development of a colorimetric method for the analysis of nickel.

Preliminary kinetic studies of the above reaction revealed that, at the trace level of nickel, the above reaction will go to near completion only if the zinc chelate is in large excess when compared with the amount of nickel in the sample. It was also found that the rate of reaction is dependent on the pH and temperature of the reaction mixture.<sup>5</sup> At a pH of 4.7 the reaction yield for a reaction period of 30 minutes increases from 68% at room temperature to about 80% at 40°C. The absorbance of the blank was also found to be minimum at the above pH. All the experiments relating to the new method of analysis were therefore, performed at a pH of 4.7 and a

temperature of 40°C using a 10<sup>-2</sup> M solution of zinc ethylenediaminetetraacetate.

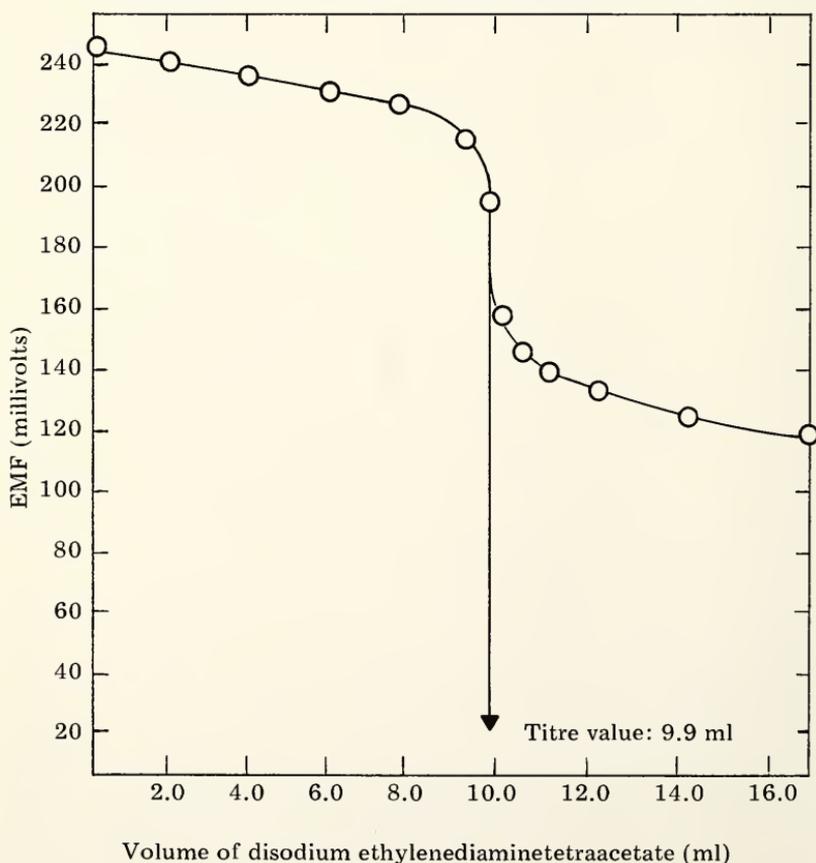
## Experimental Procedures

### Reagents

Reagent grade nickel sulfate, zinc sulfate, disodium ethylenediaminetetraacetate, carbon tetrachloride, dithizone, sodium sulfate, dimethyl glyoxime and chloroform were used in this work. All other chemicals used in this study were also of reagent grade purity. Stock solutions of nickel sulfate and zinc sulfate were standardized with a primary standard solution of oven-dried disodium ethylenediaminetetraacetate (EDTA) potentiometrically using a Hg-Hg<sub>2</sub>L<sup>2</sup> (Pt wire dipped in a mercury pool) cathode. Figure 1 shows a typical potentiometric titration curve for the titration of zinc solution. Solutions of

FIGURE 1

Potentiometric titration curve for the standardization of zinc sulfate.



lower concentrations of nickel were made from the stock solution. Other solutions used for this work are the following: Acetic acid-acetate buffer,  $3 \times 10^{-5}$  M and  $4 \times 10^{-5}$  M solutions of dithizone in carbon tetrachloride, 1% solution of dimethyl glyoxime in ethanol, 10% solution of ammonium citrate, 6 M HCl, 6M  $\text{NH}_4\text{OH}$  and 0.5 M  $\text{NH}_4\text{OH}$ . Zinc chelate (ZnEDTA) was prepared by mixing the appropriate amount of the stock solution of zinc sulfate with an equimolar quantity of the standard EDTA (sodium salt) solution and diluting with the acetic acid-acetate buffer (pH = 4.7) to 100ml to have a final concentration of  $10^{-2}$  M.

### Equipment

Thermostat, Beckman DB Spectrophotometer, Sargent Welch Recorder Model SRG and potentiometric titration assembly.

### Simplified Procedure for the Analysis of Interference Free Samples

After several control experiments changing the parameters for analysis, one at a time, the following procedure was found to be most suitable for the colorimetric analysis of nickel in interference-free samples using the nickel-ZnEDTA displacement reaction. Add 5 ml of the buffer solution (pH = 4.7) to a 25 ml test tube containing less than  $10 \mu\text{g}$  of nickel standard and dilute to 9 ml. Add 1 ml of  $10^{-2}$  M ZnEDTA and keep the reaction mixture at  $40^\circ\text{C}$  for 30 minutes. At the end of the reaction time transfer the solution to a separatory funnel containing 5 ml of  $3 \times 10^{-5}$  M dithizone in carbon tetrachloride and shake for two minutes. Collect the extract in a small beaker or test tube and dry it with a small amount of anhydrous sodium sulfate. Measure the absorbance of the clear solution at wavelengths  $536 \text{ m}\mu$  and  $620 \text{ m}\mu$ . Prepare a blank under the same experimental conditions. Repeat the experiment or run a calibration curve relating the net absorbance to the concentration of nickel in the standard. Adjust the pH of the sample solutions (3-4 ml) to about 4 and treat them in the same manner as the standard. Measure the absorbance of the samples at both  $536 \text{ m}\mu$  and  $620 \text{ m}\mu$ . Calculate the nickel content of the sample using the relation:

$$\frac{C_{\text{sample}}}{A_{\text{sample}}} = \frac{A_{\text{sample}}}{A_{\text{standard}}} \times C_{\text{standard}} \dots \dots \dots (2)$$

or directly from the calibration curve.

### Analysis of NBS Reference Standards:

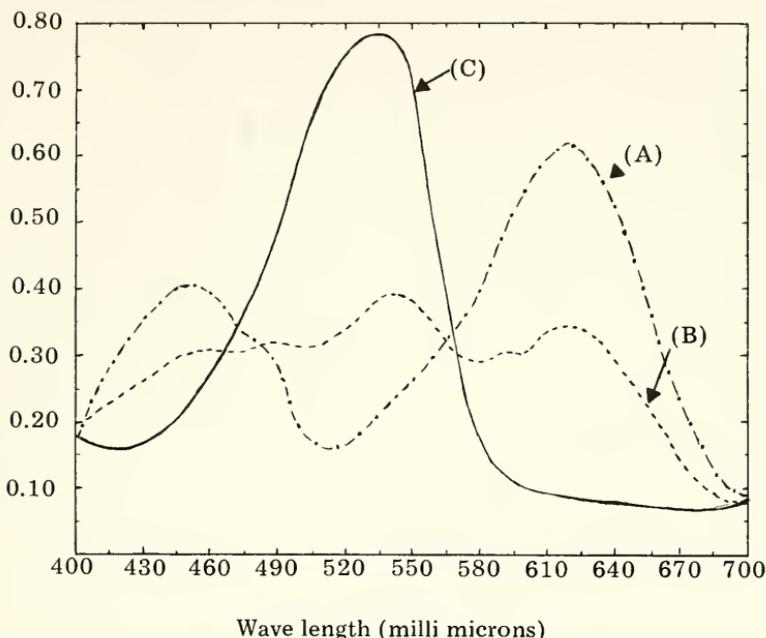
Two reference standards supplied by the National Bureau of Standards were used to test our procedure for the colorimetric analysis of traces of nickel. In a similar work conducted in our laboratory for the analysis of nickel using ZnEDTA labeled with  $^{65}\text{Zn}$  it was revealed that most of the transition metals as well as aluminum will interfere with the analysis of nickel.<sup>5</sup> This is because most of these metals form stabler chelates with EDTA than nickel thereby displacing zinc more readily from ZnEDTA than nickel. Since both of the standards are known to contain a few of the interfering metals it was thought that the nickel be separated first from the interferers before carrying out the analysis. The following procedure was therefore, devised to measure the nickel content of any sample containing interferers. Appropriate amounts of the samples are dissolved in HCl-HNO<sub>3</sub> or HF-HNO<sub>3</sub> mixtures and diluted to 100 ml in volumetric flasks. Take 1 ml or an aliquot of the sample solution containing not more than 10  $\mu\text{g}$  of nickel and precipitate the hydroxides of the interfacing elements with excess of ammonium hydroxide. Centrifuge, filter and collect the filtrate in a 25 ml test tube. Wash the precipitate one time with 0.5 M NH<sub>4</sub> OH and add the washing to the original filtrate. Acidify the filtrate and add 5 ml of 10% ammonium citrate. Neutralize with conc. NH<sub>4</sub> OH, add a few drops in excess (pH >7.5) and dilute to 20 ml. Add 2 ml of 1% solution of dimethyl glyoxime in ethanol, mix and extract with two 3 ml portions of chloroform, shaking for 30 seconds each time. Wash the combined extract two times with 5 ml of 0.5 M NH<sub>4</sub> OH.<sup>4</sup> Return nickel to the ionic state by shaking the chloroform extract with 5 ml of 6 M HCl. Evaporate the back-extract to dryness and mix the residue with 3 ml of water including washing. Determine nickel in the separated sample by the procedure outlined before. Prepare the standards and the blanks by subjecting them to the same separation, reaction and extraction procedures as before.

## Results and Discussion

In this new procedure the determination of traces of nickel in the sample is based upon the measurement of the net absorbance of the released zinc extracted into a solution of dithizone in carbon tetrachloride, at 536  $m\mu$ . Figure 2 gives the absorption spectra of the solution of dithizone in carbon tetrachloride (A), of the blank (B) and of the zinc dithizonate (C) prepared under the previously outlined experimental conditions. It is quite obvious from this figure that the gross absorbance ( $A_g(536.S)$ ) of zinc dithizonate at 536  $m\mu$  consists of contributions from the unreacted dithizone, impurities in the blank as well as from the released zinc. The net absorbance at 536  $m\mu$  due to the released zinc alone from any sample may,

FIGURE 2

Absorption curves for dithizone solution in  $\text{CCl}_4$ , blank and for zinc dithizonate; (A) Dithizone in  $\text{CCl}_4$ , (B) blank and (C) zinc dithizonate.



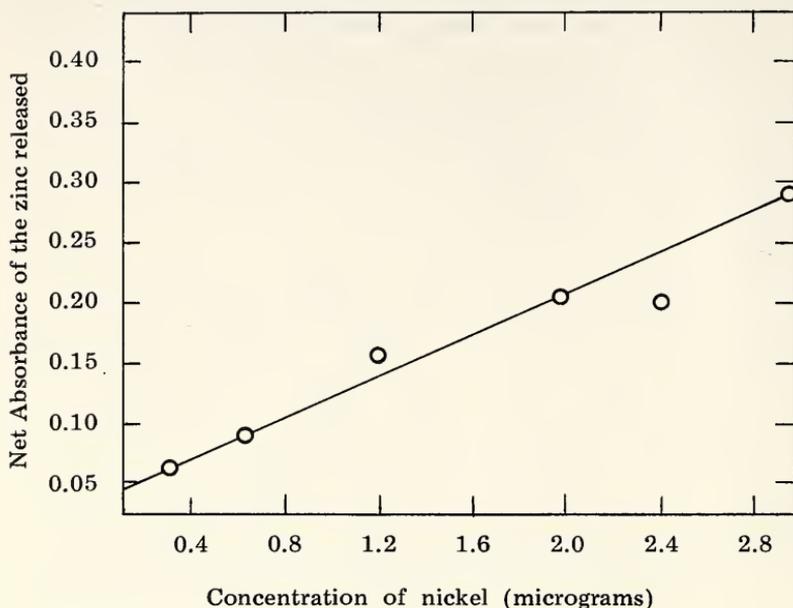
however, be obtained from the observed absorbances at  $536 \mu$  and  $620 \mu$  using the following relation:

$$A_n(536,S) = A_g(536,S) - A_g(536,b) - \frac{A_{536,DZ}}{A_{620,DZ}} (A_g(620,S) - A_g(620,b)) \dots (3)$$

where  $A_n(536,S)$  is the net absorbance of the zinc released by any given sample at  $536 \mu$ ,  $A_g(536,b)$  is the gross absorbance of the blank at  $536 \mu$ ,  $A_{536,DZ}$  and  $A_{620,DZ}$  are the measured absorbances of dithizone at  $536 \mu$  and  $620 \mu$ , respectively and  $A_g(620,S)$  and  $A_g(620,b)$  are the respective absorbances of zinc dithizonate and blank at  $620 \mu$ . The calibration graph relating the net absorbance of the released zinc and the concentration of the nickel in several standards containing various amounts of nickel is shown in Figure 3. All absorbances were measured using 1 cm cells in Beckman DB spectrophotometer. Although the calibration graph is fairly linear occasional deviations from linearity have been observed. These deviations are believed to result from contamination of the sample from zinc commonly present in glasswares, paper towels, soap and so forth. Such contamination will not affect the results in the radiochelometric method reported elsewhere.<sup>5</sup>

FIGURE 3

Calibration graph for the colorimetric analysis of nickel using Ni- ZnEDTA displacement reaction.



The sensitivity of the method as observed by our experiments is about  $0.3 \mu\text{g}$  which is much higher than what has been reported elsewhere.<sup>4</sup> Unless adequate precautions are taken to avoid contamination, the error of the analysis can, however, run as high as 10%. With the zinc chelate reagent concentration specified in this procedure one can measure nickel up to  $10 \mu\text{g}$ . For the determination of the higher concentration of nickel in the sample a more concentrated reagent has to be prepared.

Table 1 shows the results of the analysis of the NBS reference standards. It is seen from this table that the blank for the separated samples is much higher than that for unseparated samples. This appears to be the cumulative effect of the metallic impurities present in the reagents used for separation. Although significant difference is noticed between duplicate measurements, the average values are in general agreement with the average values certified by NBS. It is interesting to note, however, that the analytical results reported by different analysis show considerable deviations.

In summary, this work demonstrates that the metal-chelate displacant reactions may be used to develop suitable methods of analysis of certain metals. One of such methods for the analysis of nickel is presented.

TABLE 1

Results of the Analysis of NBS Reference Standards for Nickel  
Using the Metal-Chelate Displacement Reaction

Standards Standards Used	Absorb- ance, gross (536 m $\mu$ )	Net Ab- sorbance (536 m $\mu$ )	Amt. of Nickel ( $\mu$ g)	% Nickel (this work)	% Nickel NBS certified
Blank (Unseparated)	0.469	0.286	—	—	—
Standard (Unseparated)	0.854	0.461*	5.87	—	—
Blank (Separated)	0.727	0.595@	—	—	—
Standard (Separated)	1.153	0.528@	5.87	—	—
Ferrosilicon	1.156	0.561	6.25	0.041	
SRM 59a	0.931	0.336	3.72	0.025	
			Average: 0.033		0.028-0.039(0.033)
Aluminum Alloy	1.030	0.435	4.83	0.080	
SRM 85b	0.995	0.400	4.45	0.074	
			Average: 0.077		0.077-0.091(0.084)

\*The net absorbance of the standards and samples were obtained by subtracting the blank net absorbance from the corrected gross absorbances.

@These are averages of duplicate measurements.

## Acknowledgement

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## Footnotes

<sup>1</sup> A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc. Englewood Cliffs, N.J., 5th Edition, 1962.

<sup>2</sup> M. P. Menon, *J. Radioanal. Chem.*, *14*, 63 (1973).

<sup>3</sup> M. P. Menon, *Anal. Chem. Acta*, *64*, 151 (1973).

<sup>4</sup> E. B. Sandell, "Colorimetric Metal Analysis," Interscience Publishers, Inc., New York, N.Y., Third Edition, 1961.

<sup>5</sup> Ruth A. German, David L. Hamilton and M. P. Menon, "A Radiochelometric Method for the Determination of Traces of Nickel Using an Inorganic Displacement Reaction." Paper presented at 2nd Rocky Mountain ACS Regional Meeting, Albuquerque, New Mexico, July 8-9, 1974.