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USE OF RADIOACTIVE TRACERS IN CHEMICAL REACTIONS. DISPLACEMENT OF ZINC-NICKEL COMPLEXES FOR QUANTITATIVE DETERMINATION OF NICKEL(*)

Barbara Paci and Mitiko Saiki

ABSTRACT

In the present paper a method for the determination of small quantities of nickel by using radioactive tracers is presented.

An analytical application of the displacement reaction between nickel and zinc-ethylenediaminetetraacetate, (Zn-EDTA), labelled with ^{65}Zn is investigated.

This method is based on the extraction of radioactive zinc, displaced by nickel from the zinc chelate, into a dithizone-carbon tetrachloride solution and the subsequent measurement of the activity of an aliquot of the extract.

It is shown that the method is very sentitive and nickel can be measured in concentrations as small as 0,1 μg/ml or even less, depending on the specific activity of the radioreagent used.

The precision and accuracy of the method are determined.

The problem of interferences, trying to eliminate them by using masking agents or by means of a previous separation between nickel and other interfering metals, is also investigated.

INTRODUCTION

The purpose of the present paper is to study an analytical application of the complex displacement reaction, for the determination of traces of nickel, by using a radioreagent. This radioreagent method or radiotracer displacement method has been the subject of several studies[8] and it has been useful in trace analysis of a number of substances.

The idea of this work arose from the necessity of determining traces of nickel which usually occurs as an impurity in several materials of interest, as for example: alloys, steel, high purity metals, petroleum and also in food products[3,4,6,7].

Nickel can be present as impurity also in many nuclear materials and, in such cases, its determination is very useful in nuclear technology development. Uranium samples, including metallic uranium and other compounds like uranyl nitrate and sodium diuranate, present traces of nickel as impurity.

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One of the analytical methods employed for nickel determination in different uranium samples consists in its activation analysis with chemical separation[1].

However, the instrumental activation analysis method is not used frequently for nickel determination in uranium samples, because of the high level of radioactivity caused by the fission products and by ^{239}Np formed in the irradiated samples. Besides that, the activity induced in nickel present is very low when compared to the other activities coming from the sample.

On the other hand, a large number of analytical methods employed for the nickel determination does not lead to satisfactory results when a high sensibility is desired. In this instance, the sensitivity of the spectrophotometric technique, usually employed in analysis of microquantities of nickel is about five micrograms[10]

The activation analysis method is not advantageous for the determination of this element, because of the poor nuclear characteristic of the nickel isotopes for neutron irradiation.

An analytical method using radioreagent would be able to provide highly sensitive results for the nickel determination at trace level. This method, which is based in the work of German et al[5], consists in measuring the activity of zinc displaced from the zinc chelate, labelled with ^{65}Zn, by nickel ion. The zinc displaced is separated from the zinc chelate (Zn-EDTA), present in the aqueous solution, by means of its extraction into a dithizone-carbon tetrachloride solution. The radioactivity of the zinc displaced is proportional to the concentration of nickel in the sample.

The chemical reactions involved in the determination of traces of nickel by using solution of Zn-EDTA labelled with ^{65}Zn as radioreagent, can be represented by the following equations:

$$Zn^{*}(H_2O)_{6(aq)}^{2+} + Y_{(aq)}^{4-} \rightleftarrows Zn^{*}Y_{(aq)}^{2-} + 6H_2O \quad (1)$$

$$Ni(H_2O)_{6(aq)}^{2+} + Zn^{*}Y_{(aq)}^{2-} \rightleftarrows Zn^{*}(H_2O)_{6(aq)}^{2+} + NiY_{(aq)}^{2-} \quad (2)$$

$$Zn^{*}(H_2O)_{6(aq)}^{2+} + 2HDz_{(org)} \rightleftarrows Zn^{*}Dz_{2(org)} + 2H^{+}_{(aq)} \quad (3)$$

where

Y^{4-} represents the ethylenediaminetetraacetate ion;

HDz represents the dithizone molecule and the indexes aq and org refer to the compounds present in the aqueous and organic solutions, respectively.

The equilibrium shown by equation (1) refers to the preparation of the radioreagent; equation (2) represents the displacement reaction that occurs between nickel ion and zinc chelate of ethylenediaminetetraacetic acid; and equation (3) represents the extraction of zinc by dithizone.

Since the stability constants for the nickel complex and zinc complex of ethylenediaminetetraacetic acid (Ni-EDTA, $\log K_f = 18.62$; Zn-EDTA, $\log K_f = 16.50$)[11] differ by more than one hundred, the reaction represented by equation (2) may be used to determine nickel because the zinc released can be estimated accurately. On the other hand, the reaction represented by equation (3) may be used with success if the separation between Zn and Zn-EDTA by solvent extraction technique is complete. The zinc displaced must be completely extracted into the organic solution, while the zinc chelate must remain in the aqueous phase. The reaction can be utilized because nickel and zinc, that are present in aqueous solution as chelates, (Ni-EDTA and Zn-EDTA), do not form complexes with

dithizone. This fact can be explained by means of the stability constants values for the nickel and zinc complexes with dithizone. These values are $\log K_f = 5.83$[12] for $NiDz_2$ and $\log K_f = 6.18$[12] for $ZnDz_2$, which are smaller than the stability constants values for zinc and nickel complexes with EDTA.

EXPERIMENTAL

Preparation of the Radioreagent Solution, Zn-EDTA

For preparing the radioreagent solution zinc powder was irradiated during nearly 400 hours under a thermal neutron flux of about $10^{13} n.cm^{-2}.sec^{-1}$. The radioreagent solution was obtained by adding a standardized solution of $ZnSO_4$ labelled with ^{65}Zn, acetic acid – sodium acetate buffer solution (pH = 4.70) and a standardized solution of Na_2-EDTA.

To prevent the reaction of the added nickel with any unreacted EDTA, without displacing zinc from the Zn-EDTA complex, the quantity of zinc added for preparing the radioreagent solution was always higger than the EDTA quantity. The contribution due to this slight excess of zinc was eliminated by carrying out a blank in the same conditions, but with no nickel added.

Preliminary Experiments

The purpose of this preliminary experiments was to establish the best experimental conditions for the development of the present analytical method.

1 – Effect of Temperature and Shaking Time on the Displacement Reaction

It was verified that both temperature and shaking time affect the displacement reaction between zinc and nickel.

The results obtained in the study of dependence of the shaking time of the reactants on the product radioactivity can be seen in Figure 1. Regarding the temperature influence, a yield of 53% of displacement was found when the reaction was carried out at 24°C, and of 93% when it was carried out at 40°C. Therefore, a shaking time of 30 minutes and temperature of 40°C were chosen as the operating conditions in this work.

2 – Effect of pH on the Zinc Dithizonate Extraction and on the Displacement Reaction

It was verified that the pH value of aqueous solution affects both, the zinc dithizonate extraction and the displacement reaction. The zinc extraction was complete in the pH range between 3.30 and 5.30, however the displacement reaction yield is maximum only when the pH is between 4.50 and 4.80.

The results of these studies are presented in Tables I and II.

3 – Effect of Zinc and Dithizone Concentrations Ratio on the Percentage of Zinc Extraction

The results concerning the zinc extraction dependence on the ratio between zinc and dithizone concentrations are presented in Table III. It can be seen that only when the dithizone concentration is about ten times higher than the zinc concentration in aqueous solution, the zinc extraction is complete.

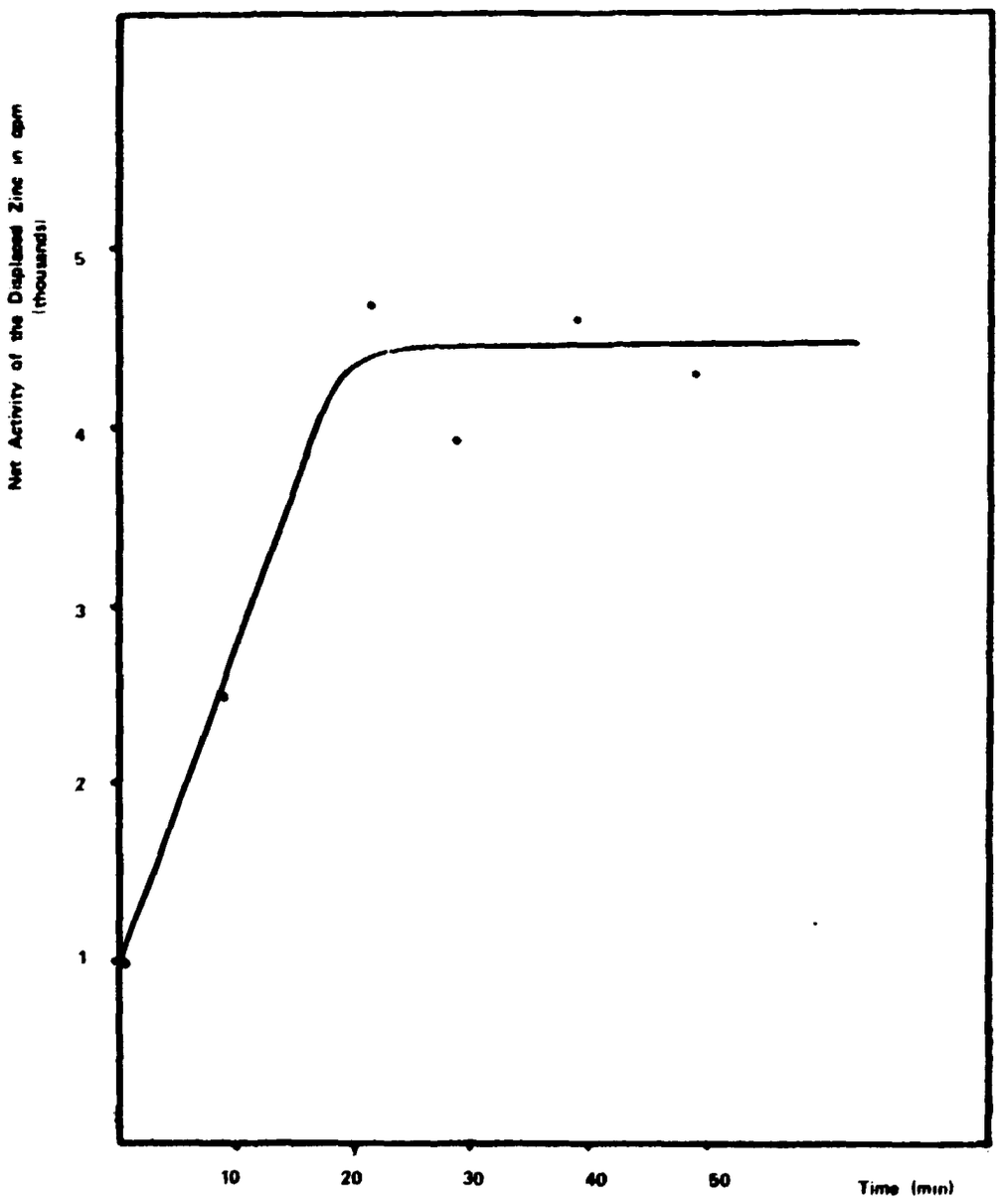

Figure 1 – Dependence of the Product Activity on the Time After Mixing the Reactants
$[Ni] = 1.4 \times 10^{-5}$ M
[Zn-EDTA] / [Ni] = 51
$[HD_2] = 10^{-3}$ M
pH = 4.70
Temperature = 40°C

Table I

Effect of pH on the Extraction Percent (% E) of Zinc

pH	% E
2.90	93.9
3.35	99.4
4.00	99.7
4.15	99.9
4.60	99.9
4.90	99.8
5.25	99.8

Experimental Conditions

Zinc concentration = 9.9×10^{-5} M
Dithizone concentration = 10^{-3} M
Shaking time for the extraction = 2 min

Table II

Effect of pH on the Blank and on the Released Zinc Activities

pH	Blank Activity (cpm)	Released Zinc Activity (cpm)
3.70	14064	_ (*)
4.30	11156	2176
4.50	7845	3798
4.80	9181	3738
5.30	8670	1732
5.40	7002	1891
5.90	7224	829

(*) Means that the blank radioactivity and nickel sample radioativity were the same, within the experimental errors of counting.

Experimental Conditions

Zinc concentration = 6.4×10^{-4} M
EDTA concentration = 6.1×10^{-4} M
Nickel concentration = 1.1×10^{-5} M
Dithizone concentration = 9.7×10^{-4} M
Temperature during displacement reaction = 40°C
Shaking time during the displacement reaction = 30 min
Shaking time for the extraction = 2 min

Since the dithizone is only slightly soluble in carbon tetrachloride (2.5×10^{-3} M[13]) a high concentration of zinc can not be used.

Table III

Effect of Ratio Between Zinc and Dithizone Concentrations (C) on Extraction Percent (% E) of Zinc

C_{HDz}/C_{Zn}	% E
2	12
4	83
6	90
8	94
12	99
20	100

Experimental Conditions

pH of aqueous solution	= 4.70
Shaking time during the extraction	= 2 min
Dithizone concentration	= 2×10^{-4} M to 10^{-3} M
Zinc concentration	= 5×10^{-5} M to 2×10^{-4} M

4 – Effect of Nickel and Radioreagent (Zn-EDTA) Concentrations Ratio on the Yield of the Displacement Reaction

The results obtained concerning the effect of the ratio between radioreagent and nickel concentrations on the yield of the displacement reaction presented in Table IV, show a great increase on this yield when the ratio increases from 2 to 54. In spite of the fact that the stability constants values for the Zn-EDTA and Ni-EDTA complexes differ by more than one hundred times, the results of Table IV show that for obtaining better yields for the displacement reaction it is necessary to use a radioreagent concentration at least 50 times higher than the nickel concentration.

5 – Dependence of the Zinc Dithizonate Extraction on the Shaking Time

The shaking time required for zinc dithizonate extraction is very short and it was observed that two minutes of manual shaking are enough for the complete extraction.

Table V shows the results obtained.

6 – Study of the Possibility of Zn-EDTA Extraction into Dithizone-Carbon Tetrachloride Solution

It was observed that Zn-EDTA complex is not extracted into a dithizone-carbon tetrachloride solution. Only the excess of zinc ions and the displaced zinc present in the aqueous solution are extracted into the organic solution as the dithizonate complex.

Table IV

Dependence of the Yield of The Displacement Reaction on the Ratio Between Nickel and Zn-EDTA Concentrations (C)

$C_{Zn\text{-}EDTA}/C_{Ni}$	Reaction Yield (%)
2	41
22	54
30	73
46	82
54	97
108	97
185	101
366	100

Experimental Conditions

pH of aqueous solution = 4.70
Shaking time for the displacement reaction = 30 min
Shaking time for the extraction = 2 min
Dithizone concentration = 10^{-3} M
Temperature during displacement reaction = 40°C

Table V

Results of Activity of Zinc Extracted as Function of Shaking Time of Extraction

Shaking Time (min)	Activity of the Zinc Extracted (cpm)
2	14442
5	14137
10	14162
15	14368

Experimental Conditions

Dithizone concentration = 10^{-3} M
Zn-EDTA concentration = 9.5×10^{-4} M
Zinc Concentration = 9.8×10^{-4} M

Experimental Procedure

Based on the conclusions obtained in the preliminary experiments, the following experimental procedure was chosen.

A solution containing radioreagent (Zn-EDTA), acetic acid – sodium acetate buffer solution and a well known volume of standard nickel solution, was prepared. This mixture was then shaken in a thermostat to allow a complete displacement reaction between zinc and nickel.

The zinc released and the excess of zinc present in the aqueous solution were extracted into a dithizone-carbon tetrachloride solution. The activity of an aliquot of the organic extract was measured by using a Nuclear Chicago single channel analyser coupled to a well-type 5.1 cm x 4.5 cm NaI(Tl) scintillation detector.

The activity of the zinc released was then determined by subtracting the activity arising from the blank from the activity found in the sample.

Calibration Curve

The calibration curve for the analysis of nickel by using the radioactive tracer displacement method, consists in plotting the net radioactivity of zinc versus nickel concentration.

To build up this calibration curve, several experiments were carried out by using known concentrations of nickel present in a series of artificial samples.

Figure 2 shows this calibration curve.

The least square method[2,9] was used to determine the slope, (a), of the calibration curve, the value of the intercept of the straight line, (b), their respective standard deviations (σ_a σ_b) as well as the correlation coefficient, (c). The values obtained for these parameters are:

$a = 7709$ $\quad b = 85$ $\quad c = 0.999$

$\sigma_a = 44$ $\quad \sigma_b = 147$

The value of the correlation coefficient determined was close to one, and this indicates a good linear correlation between the activity of the zinc released and nickel concentration within the concentration range studied.

Precision and Accuracy of the Method

In order to investigate the precision and accuracy of this method, the statistical parameters[2,9] of the data were determined.

The standard deviation of a single result(s), the arithmetic mean ($\bar{x}$), the relative standard deviation ($s_{rel} = \frac{s}{\bar{x}} \cdot 100$), the relative error ($error = \frac{\bar{x} - \mu}{\mu} \cdot 100$, where μ is the "true value") and the standard deviation of the mean ($s_{\bar{x}}$) are presented in Table VI.

The relative standard deviation determined when a 1.3×10^{-3}M nickel solution is used was lower than 8.0%, which is generally considered as a good result in trace analysis. On the other hand, the

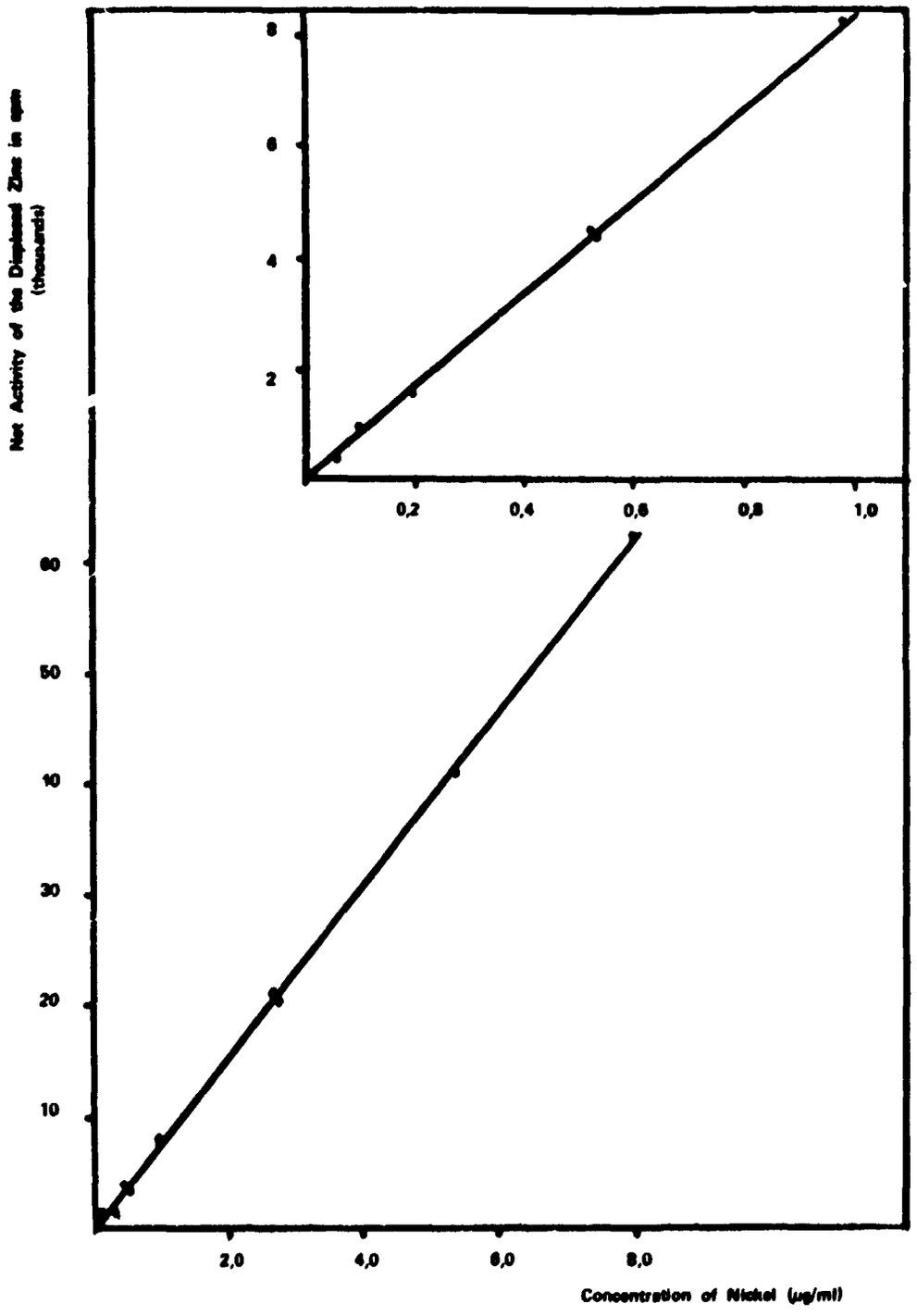

Figure 2 Calibration Curve for the Analysis of Nickel Using the Radioactive Tracer Displacement Method
[Zn-EDTA] = 5.0×10^{-3} M
[HD_z] = 10^{-3} M
pH = 4.70
Temperature = 40°C
Shaking-time during the displacement reaction = 30 min
Specific activity of the radioreagent = 4.6×10^{6} cpm/mmol

accuracy of the method, as measured by the relative error, was always lower than 5.8%. Also this result is perfectly acceptable for the analysis of microquantities.

Table VI

Study of the Precision and Accuracy of the Method

Activity of the Displaced zinc (cpm)			Blank Activity (cpm)
$C_{Ni} = 4.6 \times 10^{-6}$ M	$C_{Ni} = 1.3 \times 10^{-5}$ M	$C_{Ni} = 3.6 \times 10^{-5}$ M	
1853	4274	14143	20534
1845	3844	14083	20395
1852	3482	13918	19076
1804	3882	14147	20368
		13660	
$\bar{x} = 1865$	$\bar{x} = 3870$	$\bar{x} = 13990$	$\bar{x}_b = 20093$
$s = 66$	$s = 324$	$s = 207$	$s_b = 682$
$s_{\bar{x}} = 33$	$s_{\bar{x}} = 162$	$s_{\bar{x}} = 92$	$s_{\bar{x}_b} = 341$
$s_{rel} = 3.5\ \%$	$s_{rel} = 8.0\ \%$	$s_{rel} = 1.5\ \%$	$s_{rel} = 3.4\ \%$
error = 1.0 %	error = 2.1 %	error = 5.8 %	

INTERFERENCE STUDIES

Since, very frequently, the nickel to be analysed is present in the sample in microgram quantities, the several metals present in micro or macro-quantities interfere in the analysis.

It was then necessary to study also these interfering metals by trying to eliminate them, in order to make the present method suitable for use.

These metals interfere by displacing zinc from Zn-EDTA, or, when present in high concentration, in the completeness of the extraction of the zinc released by nickel. The dithizone-carbon tetrachloride solution may extract preferentially the interfering metal instead of the displaced zinc. This occurs when the extraction constant of the complex formed between interfering metal and dithizone is higher than that of zinc-dithizonate.

The study on the application of this radioreagent method in artificial samples containing interfering metals was made by two ways:

- by using suitable masking agents and
- by making previous chemical separation between nickel and interfering metals.

1 – Interference Study by Using Masking Agents

The method utilizing masking agents consists in chosing a suitable reagent which prevents the reaction between the interfering metal and the radioreagent, (Zn-EDTA).

The masking agent added reacts with the interfering metal by forming stable complexes or by changing the oxidation state of the interferer. Therefore, the masking agent utilized must form with the interfering metal a complex with stability constant higher than that of the complex formed between the interferer and EDTA, or change the oxidation state of the interfering metal, thus preventing its complexation with EDTA.

Moreover, the masking agent utilized in this radioreagent method must not complex nickel and the zinc displaced.

The results obtained in the experiments carried out with samples containing interfering elements, in the presence and in the absence of masking agents can be seen in Table VII. In this Table, the radioactivity of the released zinc obtained without use of masking agents show that, except for magnesium, all the elements studied interfere in nickel analysis.

The results obtained by using masking agents indicate that the problem of interference my be solved by an appropriate addition of these agents. Only for the interference of the ferric ion the masking agent used was not effective.

Magnesium does not interfere because the stability constant of the complex Mg-EDTA ($\log K_f = 8.69$)[11] is smaller than the stability constant of the Zn-EDTA complex.

2 – Interference Study with Previous Nickel Separation

In this case, the nickel had to be separated from the interfering elements before the addition of the radioreagent.

The analytical method that makes use of dimethylglioxime presented by Sandell[10] was applied for this separation.

This separation provides the isolated nickel in the ionic form (Ni^{2+}), suitable for the application of the radioreagent method, since Ni^{2+} is back-extracted from the complex previously formed with dimethylglioxime.

The loss of nickel during the separation procedure must be very small, in order to get a high separation yield and subsequent satisfactory nickel determination.

Table VIII shows the mass of interferer utilized and also the mass of nickel determined after chemical separation from the interfering elements.

The mass of nickel obtained was slightly higher or lower than the mass of nickel utilized in all the experiments (3.76 μg).

The major source of this error is, probably, the loss of nickel during the chemical separation and the incomplete separation of the nickel from the interfering element.

Table VII

Displaced Zinc Activity in the Presence of Interfering Metals and of Masking Agents

Mass of interferer	Mass of masking agent	Activity(*) (cpm)	Activity(**) (cpm)
–	–	4859	–
1 mg of Mg^{2+}	–	5411	–
1 mg of Cu^{2+}	100 mg thiourea	20343	10029
0.6 mg of Sn^{2+}	102 mg sodium potassium tartrate	750	5136
1 mg of Al^{3+}	50 mg sodium fluoride	80817	4982
1 mg of Cr^{3+}	100 mg ascorbic acid	15177	11337
1 mg of Fe^{3+}	4.5 mg sodium fluoride	105755	164368
0.03 mg of La^{3+}	0.91 mg sodium fluoride	27549	7017

(*) Indicates displaced zinc activity obtained without use of masking agent
(**) Indicates displaced zinc activity obtained in presence of masking agent

Experimental Conditions

Zn-EDTA concentration = 9.5×10^{-4} M
Nickel concentration = 1.6×10^{-5} M
Dithizone concentration = 10^{-3} M
pH of the aqueous solution = 4.70
Volume of aqueous phase = volume of organic phase = 5 ml
Specific activity of the radioreagent = 3.3×10^{8} cpm/mmol

Table VIII

Nickel Determination after Chemical Separation of the Interfering Metals

Mass of Interferer	Mass of Nickel Determined (μg)
–	3.77
1 mg of Mg^{2+}	3.66
1 mg of Mn^{2+}	2.99
1 mg of Co^{2+}	2.73
1 mg of Cu^{2+}	4.37
1 mg of Cd^{2+}	3.57
0.6 mg of Sn^{2+}	3.69
1 mg of Cr^{3+}	3.52
1 mg of Fe^{3+}	3.13
0.03 mg of La^{3+}	3.69

Experimental Conditions

Zn-EDTA concentration	= 9.5×10^{-4} M
Nickel concentration	= 1.3×10^{-5} M
Dithizone concentration	= 10^{-3} M
pH of the aqueous solution	= 4.70
Aqueous solution volume	= organic solution volume = 5 ml
Specific activity of the radioreagent	= 3.1×10^{8} cpm/mmol

DISCUSSION AND CONCLUSIONS

The results obtained in this work show that it is possible to use a radioactive tracer to study an analytical application of the displacement reaction between nickel and zinc of the complex Zn-EDTA, for the nickel determination.

As it was verified in the preliminary experiments, the complete displacement of zinc from the Zn-EDTA complex by nickel ion is achieved when: 1) the radioreagent concentration is at least 50 times higher than that of nickel; 2) the value of the pH of the aqueous solution is 4.70; and 3) the shaking time for the displacement reaction is of 30 minutes at a temperature of 40°C.

Besides that, it was shown that the separation between the displaced zinc and the zinc in the Zn-EDTA form, by means of the extraction with dithizone-carbon tetrachloride solution, is effective since the Zn-EDTA complex remains in the aqueous solution while the free zinc is completely extracted into the organic solution.

The sensibility of the method, that can be estimated through the calibration curve (Figure 2), is about 0.1 μg/ml of nickel.

Unlike what happens with other methods, the sensitivity of this method can be enhanced by increasing the specific activity of the radioreagent.

German et al.[5] have observed that this method gives better sensitivies than the spectrophotometric and neutron activation analysis methods.

The linearity of the method can be observed by the distribution of the points of the calibration curve and by the value of the correlation coefficient.

By applying the t-criterion[2,9] it was possible to infer, with a confidence probability of 95%, that the intercept of the straight line on the axis of ordinate can be estimated as zero. This fact shows that this method is not affected by systematic errors.

Futhermore, the results of the study of the precision and accuracy (Table VI) show that the present method is quite reproducible and accurate for the analysis of nickel present in microquantities.

The study of the problem of interferences shows that the method can be applied using suitable quantities of masking agents or carrying out a previous nickel separation.

In brief, the results obtained in this work prove that the method studied can be applied satisfactorily to determine traces of nickel, even in laboratories that do not dispose of a nuclear reactor in the nearness. Indeed, the suppling of tracer ^{65}Zn with high specific activity is enough to provide the analysis of a great number of samples.

RESUMO

No presente trabalho, estuda-se um método de determinação de pequenas quantidades de níquel, utilizando reagente radioativo como traçador.

Investiga-se uma aplicação analítica de reação de deslocamento entre o níquel e o etilenodiaminotetraacetato de zinco (Zn-EDTA) marcado com zinco-65.

Este método baseia-se na extração do zinco radioativo, deslocado pelo níquel do seu quelato Zn-EDTA, com ditizona em tetracloreto de carbono e posterior medida de atividade de uma alíquota de solução orgânica.

Demonstra-se que o método é bastante sensível e o níquel pode ser medido em concentrações da ordem de 0,1 micrograma por ml ou até inferiores, dependendo da atividade específica do reagente radioativo utilizado.

Determinam-se a exatidão e a precisão do método.

Faz-se também um estudo sobre o problema de interferências, procurando eliminá-las através da utilização de agentes mascarantes ou por meio de uma separação prévia do níquel dos demais elementos interferentes.

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INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES
Caixa Postal, 11 049 – Pinheiros
CEP 05508
01000 – São Paulo – SP

Telefone: 211-6011
Endereço Telegráfico – IPENUCLEAR
Telex – (011) 23592 - IPEN - BR