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RCN REPORT

Trace-Determination of Cadmium by
Neutron Activation.
Application to Air-Borne Particulates,
Hair and Foodstuffs.

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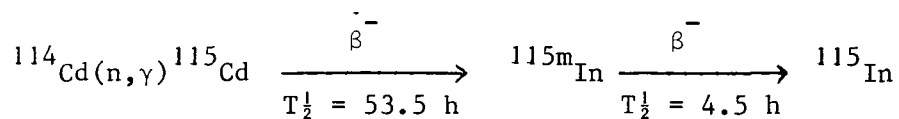
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SUMMARY

This study describes a routine-procedure by neutron activation for the determination of cadmium in industrial air-borne particulate samples, collected on filter paper, hair and foodstuffs.

The reaction used is

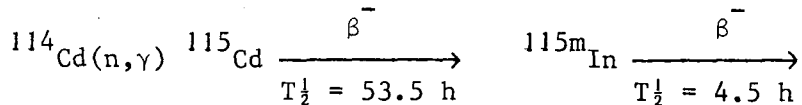


Cadmium is isolated by liquid-liquid extraction with a chloroform solution of dithizone. The activity of the ^{115}In -daughter is counted. The method was tested by analysis of the standard kale powder.*

* This material was prepared and issued by Dr. H.J.M. Bowen in 1966, to provide a reliable standard for intercomparison purposes.

1. INTRODUCTION

The determination of cadmium in samples from the biosphere has often been asked for. Air-dust, hair and foodstuffs represent common types of samples. The average concentration will seldomly exceed 1 $\mu\text{g/g}$. Consequently, a sensitive method should be available. Neutron activation using the reaction



offers a suitable possibility.

After activation for ten minutes in a thermal neutron flux of $5 \cdot 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$, the resulting activity of ${}^{115}\text{Cd}$ is $0.6 \cdot 10^2 \text{ d/sec.}\mu\text{g}$. The activity of ${}^{115\text{m}}\text{In}$ after a decay-period of 70 hours is $0.3 \cdot 10^2 \text{ d/sec.}\mu\text{g}$.

The γ -activity of the 335 keV internal transition is $\approx 0.15 \cdot 10^2 \text{ d/sec.}\mu\text{g}$.

Three types of separation techniques are described in literature.

a) Radiochemical separation by amalgam exchange [1]

This method uses the exchange-reaction of radiocadmium with cadmium-amalgam, followed by back-extraction or elution with thalious ions. The procedure is not quantitative and takes too much time for routine-purposes.

b) Anion-exchange [2]

Cadmium forms a strong anionic complex iodide which can be separated from other metals (especially zinc) by anion-exchange. Cadmium is eluted from the resin with 3 N nitric acid. This procedure was judged too time-consuming for routine applications.

c) Liquid-liquid extraction [3-7]

This technique is sufficiently rapid. Two extractants are frequently used: Dithizone [3,5,6] and diethyldithiocarbamate [4]. 8-Quinolinol is mentioned too [7]. This last reagent is too unspecific for our purposes. From initial experiments it appeared that dithizone is the most convenient extracting agent. The procedures described in literature use either cyanide [6] or rhodanide [5] as a masking complexant. It was found that these reagents can be omitted if tartrate and hydroxylamine are added [3].

2. PRINCIPLE

2.1. Sampling

The air-dust samples are collected by pumping in 24 hours $\approx 1200 \text{ m}^3$ air through a $220 \times 130 \text{ mm}^2$ microsorban filter. This is cut into rectangular pieces for various analyses. The amount of sample collected is in the order of 100 - 200 mg. The distribution of the dust over the filter-area is homogeneous. This was proved by dividing one filter in rectangular pieces of $20 \times 10 \text{ mm}^2$ irradiating for 2 minutes and comparing the count-rates of the photopeaks of ^{24}Na ($T_{1/2} = 15 \text{ h}$) and ^{56}Mn ($T_{1/2} = 2.6 \text{ h}$). For the Cd-determination $\approx 300 \text{ mm}^2$ is taken. This means an average sample-weight of 1 - 2 mg. The reason for this small sample-size lies in the destruction method used.

The hair-samples were obtained from three people working in a zinc refinery as well as from other persons. They were taken under rather unspecified conditions.

The foodstuffs were taken from the commercially available canned foods for infants. Samples of ≈ 50 gram were ashed at 450° C . As is known, this results in no appreciable loss |8|.

2.2. Method

The samples are put into a polythene or a quartz vial and irradiated for 10 minutes in the pneumatic rabbit system of the HFR at a thermal neutron flux of $5 \cdot 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$. As standards, 20 λ aliquots of a standard solution are used. After a cooling-period of 24 hours, the filter-material is burned in an oxygen atmosphere |9| in a Schöninger combustion apparatus |10|.

The absorption liquid is 2 N nitric acid to which 50 μg cadmium carrier has been added.

Sodium potassium tartrate and hydroxylamine hydrochloride are added for masking purposes. The solution is now neutralized ($\text{pH} = 8$) by addition of 5 N potassium hydroxide and made alkaline by a further addition of 5 ml 25% potassium hydroxide. Extraction is performed three times with 10 ml of a 0.002% solution of dithizone in chloroform. Apart from cadmium, cobalt, nickel, silver, gold, mercury and zinc enter the organic phase. Washing is performed with subsequent portions of 15 ml distilled water until the pH-value of the washing liquid is 8.5. Ten milliliters of a $\text{pH} = 2$ buffer are added. Cadmium and zinc are back-extracted whereas the other metals have stable dithizonates at this pH-value and remain in the

organic phase. This was proved by tracer experiments.

The addition of 10 ml buffer solution is only possible after the thorough washing mentioned above. It will result in a much smaller volume of the aqueous layer than in the procedure described in literature [3].

As 5 ml aliquots are taken for counting, this means a considerable enhancement of the sensitivity.

The aliquots are stored for ≈ 45 hours to allow the equilibrium between ^{115}Cd and $^{115\text{m}}\text{In}$ to be reached. They are counted for 10 minutes with a NaI well-type detector. The γ -ray spectra are recorded and the area under the 335 keV photopeak of $^{115\text{m}}\text{In}$ is determined.

3. EXPERIMENTAL

3.1. Chemicals and equipment

All chemicals are of p.a. quality.

A solution of 6.88 mg/100 ml $\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ in distilled water.

2 N HNO_3

5 N KOH

0.2 N HCl

0.2 N KCl) to be combined to the "Clark and Lubs" buffer-solution. *

A 20% solution of $\text{KNa C}_4\text{H}_4\text{O}_6 \cdot 4 \text{H}_2\text{O}$

A 20% solution of $\text{NH}_2\text{OH} \cdot \text{HCl}$

A 0.002% solution of dithizone in chloroform

A 0.02% solution of dithizone in chloroform

Standard solution of $\text{pH} = 4$) Beckmann

Standard solution of $\text{pH} = 10$

A 20 λ Eppendorf-micropipette

5 ml pipettes

a stove

100 ml beakers

Quartz vials (inside diameter 8 - 10 mm)

100 ml volumetric flasks

100 ml separatory funnels

(for the analysis of the

18.5 x 9.4 mm polythene vials with snap-caps

kale powder, hair and food-stuffs).

15 ml test tubes with polythene stoppers

Graduated cylinders of 10 and 25 ml.

A pH-meter.

* Note: This buffer is a 100 ml aqueous solution, containing 6.5 ml 0.2 N HCl and 25 ml 0.2 N KCl .

A Schöninger combustion oven, type "Mikro-K". Flask volume is 750 ml. A 3" x 3" NaI well-type crystal, mounted in an automatic sample-changer and connected to a 400 channel-analyzer with an IBM electrical type-writer.

3.2. Procedure

3.2.1. Air-dust samples

1. Irradiate 300 mg filter-material, packed in a polythene vial, for 10 minutes at a thermal neutron flux of $5.10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$. Cool for one day.
2. Transfer to the combustion oven, add 40 ml 2 N HNO_3 as absorption solution and 20 λ of the $\text{Cd}(\text{NO}_3)_2$ -solution.
3. Burn the sample and shake the flask for 1 minute. Then transfer the solution to a 100 ml beaker.
4. Add 5 ml of the 20% KNa tartrate solution and 1 ml of the 20% $\text{NH}_2\text{OH.HCl}$ solution. Make alkaline by addition of 5 N KOH until the pH has reached the value of 8. Add 5 ml 25% KOH solution.
5. Transfer to a 100 ml separatory funnel. Add 10 ml of the 0.002% extracting solution and shake for 1 minute.
6. Repeat the extraction two times. The aqueous layer should be brown. If not, further extraction is necessary. Combine the organic fractions.
7. Add 5 ml of the 0.02% dithizone solution to the organic phase. Wash with four subsequent 15 ml portions of distilled water. The pH-value of the last washing fraction should be 8.5. If it is higher the washing has to be continued.
8. Add 10 ml of the "Clarks and Lubs" buffer solution and shake for 2 minutes. Collect the aqueous phase in a 25 ml graduated cylinder. The volume is noted and a 5 ml aliquot is pipetted into a 15 ml test tube. The tube is closed and stored for 45 hours.
9. Count the aliquots for at least 30 minutes in the well of a 3" x 3" NaI detector. The γ -ray spectra are recorded by a 400 channel analyzer and read out in the region of interest (300-370 keV) by an IBM electrical type-writer.

3.2.2. Kale powder

1. Up to 200 mg is packed in a quartz vial, which is sealed off and irradiated for 5 x 5 minutes at a thermal neutron flux of 5.10^{13} $\text{cm}^{-2} \text{sec}^{-1}$, together with standards.

After every 5 minutes of irradiation, a cooling period of 10 minutes is observed.

The sample is then cooled for one day.

2. The quartz vials are put into a plastic "pocket" and broken.

The rest of the procedure is identical to that for the air-dust samples (steps 2 - 9).

3.2.3. Hair-samples

The procedure is identical to that for kale powder except the cooling time which is 15 hours here.

3.2.4. Foodstuffs

The procedure is identical to that for kale powder except the cooling time. Due to the high ^{24}Na - and ^{38}Cl -activities the time between irradiation and chemical isolation has to be ≈ 2 days.

3.2.5. Carrier solution and standards

1. An amount of 688 mg of $\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ is weighed out on a micro-balance, transferred to a 100 ml beaker and dissolved in 25 ml distilled water. This solution is transferred to a 100 ml volumetric flask and made up to the mark; 20 λ will contain 50 μg cadmium. The solution is used as a carrier and as a standard.
2. Standards are made by pipetting 20 λ aliquots in 18.5 x 9.4 mm polythene vials. They are irradiated simultaneously with the samples.
3. Counting is performed as for the samples. The observed count-rate in the 335 keV photopeak is $\approx 5.10^2$ counts $\text{min}^{-1} \mu\text{g}^{-1}$ for an irradiation-time of 10 minutes.

4. RESULTS

4.1. Standard kale powder

This material was analysed to get an impression of the reliability of the procedure. Bowen who issued the standard, reports 0.38 ± 0.05 $\mu\text{g}/\text{gram}$ [11]. The values found in different runs with this method are:

0.48 ± 0.05 $\mu\text{g Cd}/\text{gram}$

0.46 ± 0.05

0.51 ± 0.05

0.54 ± 0.05

The average value is 0.50 ± 0.02 $\mu\text{g}/\text{gram}$.

4.2. Air-borne particulates

Some results of the determination of cadmium in this material are:

Sample	ng Cd / m ³ air
1	5 ± 1
2	5 ± 1
3	18 ± 2
4	21 ± 2
5	51 ± 2

4.3. Hair samples

The results obtained for the samples of the three possibly contaminated persons (1 - 3) and for one of the comparison samples (4) are:

Person	Sample - weight	$\mu\text{g Cd} / \text{gram}$
1	35.0	2.4 ± 0.4
	34.3	2.2 ± 0.4
2	9.8	3.6 ± 0.5
	104.0	3.2 ± 0.5
3	57.9	21.4 ± 1.4
	123.0	27.0 ± 1.2
4	33.6	0.04 ± 0.02

4.4. Foodstuffs

No cadmium could be detected in any of the investigated samples of canned food. The reported upper limits correspond to the detection of 50 counts in 120 minutes.

<u>Material</u>	<u>Ash-percentage</u>	<u>Cadmium- concentration in the ash</u>	<u>Cadmium- concentration in the sample</u>
Beef	4.5 - 6.0	< 0.04 µg/gram	< 2 ng/gram
Carrots	6.5	< 0.05	< 3
Endive and potatoes	8.0	< 0.07	< 5
French beans	7.7	< 0.10	< 8
Lentils	2.7	< 0.08	< 2
Spinach and potatoes	12.8	< 0.04	< 5

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