

RADIOCHEMICAL SEPARATION OF ^{109}Cd AND ^{203}Hg BY ION EXCHANGE CHROMATOGRAPHY*

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ABSTRACT

NAA of mercury and cadmium in food, at trace levels, usually needs suitable methods of radiochemical separation. This work explores two of such procedures. In the first procedure an irradiated sample is heated with a mixture of sulphuric, nitric and perchloric acids under reflux conditions in presence of potassium dichromate. Mercury is isolated by retention in a small column of granulated copper, the cadmium from the sample is deposited in a strongly acid cation exchange column and eluted with 0.75 N HCl. In the second procedure the sample is heated in a Kjeldahl flask, with a mixture of sulphuric and nitric acids with periodical addition of hydrogen peroxide. The cadmium and mercury are retained in a cation exchange column and separated by selective elution. Percentage of recovery, through sample dissolution and radiochemical separation, was determined by gamma spectrometry of radiotracers as well as by EDTA titrimetry of the carriers. Tracer experiments employing Cd (109) and Hg (203), show appropriated recoveries, enabling this separations useful for NAA of such elements at trace level.

1. INTRODUCCION

Due the high toxicity of Hg and Cd, chemical analysis of such elements in food products, at trace levels, has been reported by several workers using different techniques [1-3, 5-8, 10-14, 17, 20, 23]. This elements are present in the ppb range, at these levels, uncontrolled analyte losses during sample preparation and contamination -due to impurities in the reagents- are severe shortcomings of almost all current analytical techniques. Neutron activation analysis is nearly free of these shortcomings. Generally, to avoid spectral interferences caused by the other activated elements in the matrix, the schemes employed require destruction of the irradiated sample and separation of radioisotopes produced during activation.

Chemical destruction of samples containing Hg is a topic extensively covered in the literature due the high volatility of this element and several of its compounds, which can produce

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considerable losses. Some suitable destruction techniques are the Schöniger flask combustion [21], microwave combustion [23], and wet acid attack in Bethge apparatus [3,9] or in teflon bomb [10]. All these methods give almost quantitative recoveries but expensive equipment is required. Wet methods employing simple apparatus, generally give considerable Hg losses, especially if the attack is verified in presence of HClO_4 . Feldman [8] has developed a very good method based in the combined action of HNO_3 , H_2SO_4 and HClO_4 in presence of $\text{K}_2\text{Cr}_2\text{O}_7$. The reaction takes place in an open vessel and the reported recovery is of 99.1%. Biso et al. [3] use a mixture of H_2SO_4 and fuming HNO_3 , attacking under reflux in the Bethge apparatus and heating to white H_2SO_4 fumes in the open flask.

Several techniques have been successfully employed in radiochemical separation of Hg and Cd. For instance, selective precipitation [3], distillation of volatile compounds of Hg [7,22], isotopic exchange [17], solvent extraction [10,11], ion exchange chromatography [13,16,20,2] and electrodeposition [15]. Frequently two or more separation techniques are simultaneously used [7,15,16]. Biso et al. [3] made the Hg separation by double precipitation, first as metal which is then redissolved in HNO_3 and reprecipitated as $\text{Hg}(\text{SCN})_2$. The reported recovery for the total attack - separation process is between 70 and 90%. Grimanis et al. [11], employ toluene and extract Hg bromocompounds from a 7.00M H_2SO_4 and 0.01M HBr solution. Greenberg [10] extracts Hg and Cd from biological samples, wet ashed in teflon bombs, using chloroformic solutions of diethyldithiocarbamates of Ni(II) and Zn(II). Regarding the methods by ion exchange some use has been made of the anion exchange of $\text{Hg}(\text{II})$ and $\text{Cd}(\text{II})$ chlorocomplexes [13,16], but the cation exchange of $\text{Hg}(\text{II})$ has not been completely explored, so, some publications show this possibility, Strelow [18], Usatenko and Tulyupa [19]. An attractive method for Hg isolation, employed by Valentini et al. [20] and Brandone et al. [5], is the retention by small granulated copper columns, on which the $\text{Hg}(\text{II})$ is reduced. Being the adsorption of ^{75}Se , the major potential shortcoming.

The objective of the present work was the development of a simple, quick and low cost procedure for attack-radiochemical separation; suitable for NAA of Hg and Cd in food.

2. EXPERIMENTAL PART

2.1 RADIOACTIVITY MEASUREMENTS.

All activity measurements were made by gamma spectrometry on the 21.1 KeV ^{109}Cd and 279 KeV ^{203}Hg photopeaks. Low resolution spectra were obtained with a 3" x 3" well type $\text{NaI}(\text{Tl})$ scintillation detector and, the high resolution by means of an intrinsic germanium coaxial detector and associated electronics. This system is linked to a CAMBERRA series 40 Multichannel analyzer connected to a personal computer DEC "Professional 350". Photopeaks' intensity evaluation was made by the total area method.

The continuous measurement of eluate activity were performed by means of a lead collimator in front of a scintillation detector coupled to multichannel analyzer working in multiscaling mode.

2.2 WET ASHING.

- a) HNO_3 - H_2SO_4 - H_2O_2 MIXTURE: Chemical digestion was made in 30 ml Kjeldahl flasks, under the experimental conditions shown in Table 1. 1.00 ml of $\text{Hg}(\text{NO}_3)_2$ and 1.00 ml $\text{Cd}(\text{NO}_3)_2$ standard solutions, labelled with $^{203}\text{Hg}(\text{II})$ and

Table 1: Hg recovery in spiked sample wet ashing.

% Hg RECOVERED		
CONDITIONS	HClO ₄ : 3.0 ml	H ₂ SO ₄ : 1.0 ml
	HNO ₃ : 4.0 ml	HNO ₃ : 4.0 ml
	K ₂ Cr ₂ O ₇ : 2 mg	H ₂ O ₂ : drop by drop
	Carrier: 25 mg Hg(II)	Carrier 273 mg Hg(II)
SAMPLES	10 mg Cd(II)	10 mg Cd(II)
Pig liver	90.5	95.3
higado	96.2	95.5
(100 mg)	95.8	95.5
Powdered	91.0	98.1 (*)
milk	90.1	96.4 (*)
(200 mg)	90.4	96.2 (*)

(*): Samples ashed without Cd(II).

Table 2. Hg recovery in wet ashing - separation from spiked powdered milk samples: Gamma spectrometry Vs. EDTA titration (*).

EXPERIMENT	% Hg RECOVERED	
	GAMMA SPECTROMETRY	EDTA TITRATION
Ashing: H ₂ SO ₄ HNO ₃ - H ₂ O ₂	98.1	98.1
	96.4	97.5
	96.2	96.8
Ion exchange separation.	97.7	98.3
	97.1	97.4
	98.0	97.4

(*): Samples ashed without Cd(II). Tracer and carrier added just before separation.

¹⁰⁹Cd(II) respectively, was added to each sample. The heating was gradually increased to white fumes, with periodical addition of H₂O₂, until the remaining solution was completely colorless. After cooling, the volume was adjusted to 50.0 ml in a volumetric flask. Standard solutions, for comparison purpose, were made

Table 3. Cadmium recovery by ion exchange separation: Gamma spectrometry Vs. EDTA titration (synthetic samples treated as table 4 shows).

COLUMN DEPOSITION	% Cd(II) RECOVERED	
	GAMMA SPECTROMETRY	EDTA TITRATION
0.1M HNO ₃	96.5	99.2
	97.0	99.5
	94.8	99.2
0.1M HClO ₄	95.3	99.5
	96.4	99.0

adding 1.00 ml of each, the standard Hg(II) and Cd(II) labelled solutions, and 1.00 ml H₂SO₄ to a 50 ml volumetric flask, adjusting the volume with distilled water. The recovery was found by gamma spectrometry measurements on 2.00 ml aliquots of sample and standard solutions. Data shown in Table 2. was obtained by 0.01M EDTA titrimetry on 10.00 ml aliquots of standard and sample solutions. Xilenol orange was used as indicator and the pH was kept at 6.00 by means of urotropine buffer.

- b) HNO₃ - HClO₄ - K₂Cr₂O₇ mixture: The adopted procedure may be regarded as a quite licentious version of FELDMAN's method. Chemical digestion was made in a 25 ml conical flask attached to a 32 cm air cooled condenser. Table 1 shows the experimental conditions. To begin, the sample plus acid mixture were heated to soft boiling until the emission of red fumes has completely ceased and the solution turned to emerald green color. Then the temperature was rised cautiously step by step, heating just until solution turns to bright orange. Afer cooling, the volume of the remaining solution was adjusted to 100.0 ml in a volumetric flask. Comparison solutions were made adding 1.00 ml of each labelled standard solution, 2.00 mg of K₂Cr₂O₇ and 3.0 ml of HClO₄ to a 100 ml volumetric flask, then the volume was adjusted with distilled water. Finally, 25 ml aliquots of samples and standards were measured using a NaI(Tl) radiation detector attached to a gamma spectrometer. The samples, for gamma measurements, were deposited on plastic petri dishes and counted on a fixed geomatry by means of acrylic sample holders.

2.3 Hg(II) - Cd(II) SEPARATIONS BY ION EXCHANGE.

- a) QUANTITATIVE SEPARATIONS: Chromatographic experiments were performed using 15 cm high and 1.0 cm cross section glass columns with sintered glass discs at the bottom, packing was made with 10 ml (3g dry weight) 200-400 mesh AGW50-X8 resin, conditioned in usual way. Flow rate was kept at 1.0 ml/min. in all experiments, Table 4. shows the type of samples and other experimental conditions. Recovery was found by both, gamma spectrometry and 0.01M EDTA titrations on collected fractions and standard solutions.

- b) **ELUTION CURVES:** For Hg(II) and Cd(II) from synthetic mixtures, elution curves were obtained at the experimental conditions shown in Table 4, eluate radioactivity being continuously measured. For Hg(II) and Cd(II) from powdered milk spiked samples, elution curves were obtained passing 10.00 ml of our "sample solution" through the column, washing with 150 ml of 0.5 N H₂SO₄ and eluting with, 0.16N (Hg) and 0.64N (Cd), HCl solutions. 2.5 ml fractions were collected in polyethylene vials and counted in the well type detector. All separations were designed according to distribution coefficients published by Strelow [8].

Table 4: Hg(II) – Cd(II) recovery by ion exchange separation (data from gamma spectrometry).

SAMPLE	ASHING	DEPOSITION ON COLUMN:	ELUTION (50ML/ION)	% RECOVERED	
				Hg(II)	Cd(II)
Pig liver (100 mg)	HClO ₄ + HNO ₃ K ₂ Cr ₂ O ₇	100 ml HClO ₄ 0.3N, wash: 20 ml HClO ₄ 0.1N	0.2N HCl	44.2	95.8(*)
			Hg(II).	57.8	95.3(*)
			0.5N HCl Cd(II).	46.3	94.6(*)
Powdered milk (200 mg)				48.7	94.3(*)
				51.6	85.5(*)
				47.1	96.0(*)
Powdered milk (200 mg)	H ₂ SO ₄ + HNO ₃ + H ₂ O ₂ .	50 ml H ₂ SO ₄ 0.5N, wash: 150 ml H ₂ SO ₄ 0.5N	.16N HCL:	97.7	99.1
			Hg(II).	97.1	98.6
			.64N HCl: Cd(II).	98.0	99.5
Synthe- tic mixture	None 0.1N, wash: 20 ml	100 ml H ₂ SO ₄ Hg(II). 0.5N HCl: HNO ₃ 0.1N	0.2N HCl:	98.0	96.5
				99.7	97.0
			Cd(II).	98.2	94.8
10 mg Cd(II), 25 mg Hg(II).		100 ml HClO ₄ 0.1N, wash: 20 ml HClO ₄ 0.1N		99.1	95.3
				97.5	96.4

(*): Cd data from wet ashing - separation whole process.

2.4 Hg(II) SEPARATION ON GRANULATED COPPER.

Eppendorf micropipet tips, with a cotton plug at the bottom, containing 1.0 cm high bed of granulated copper were used as retention column. Each sample was wet ashed with 5.0 mg Hg(II) as a carrier and 2.00 KBq of $^{203}\text{Hg(II)}$ tracer. Sample solutions were passed through columns at 2.0 ml/min flow rate, and the whole column activity measured in the well type detector. Comparison standards were prepared depositing 2.00 KBq of the tracer and 5.0 mg of the carrier in similar columns.

2.5 Hg(II) SEPARATION FROM IRRADIATED SAMPLES.

Six powdered milk samples (300 mg each) contained in quartz ampoules were irradiated in a 2×10^{13} n/cm.s thermal neutron flux for 20h at the Universidade de Sao Paulo (Brasil) nuclear reactor. This experiment was only for qualitative purposes and so no standards were included. After 45 days the samples were placed in polyethylene vials and the high resolution gamma spectra obtained. Each sample was wet ashed as described in [2.1.b], being necessary to add 1.00 ml of H_2SO_4 , otherwise the reaction of HClO_4 and remaining organic matter was extremely violent in the last step of ashing. Sample solutions were passed through granulated copper columns and counted at the HP(Ge) detector.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Table 1 shows that chemical yields of the two wet ashing procedures are potentially useful for quantitative NAA. The observed Hg losses in presence of HClO_4 may be due to differences between our heating - refluxing conditions and the Feldman prescription [8]. The Hg losses are always smaller than those reported by Gorsuch [9]. Chemical yield, employing the H_2SO_4 - HNO_3 mixture seems to be better for powdered milk samples and as in the case of HClO_4 mixture for pig liver. Fat is not fully wet ashed by H_2SO_4 - HNO_3 - H_2O_2 mixture [9], however this should not be a serious drawback as long as irradiation brings organic Hg into Hg^0 , Hg_{2+2} , or Hg^{+2} species [6].

As shown in Table 2 and 3; EDTA complexometry is useful, for recovery determinations, for the sample dissolution - radiochemical separation step. The observed discrepancy for Cd(II) in table 3, and the slightly low recoveries shown in table 4, may be due to a systematic error in the 21.1 KeV ^{109}Cd photopeak measurement. Counting procedure was improved for the H_2SO_4 - HNO_3 - H_2O_2 experiments, and so very good results were obtained.

Chemical yields of Hg(II) - Cd(II) by ion exchange separations arising from spiked samples of powdered milk, pig liver and synthetic mixtures, are shown in table 4. The serious Hg losses, observed for samples wet ashed with HClO_4 mixture were due to poor retention in the chromatographic columns. Chloride elimination, from the sample solutions by precipitation with AgNO_3 , showed that losses are due to Hg(II) chlorocomplex formation. These are not retained by the column (The chloride ions are originated by HClO_4 degradation). For the case of synthetic mixtures and samples wet ashed without HClO_4 the results are practically equal and, though not strictly quantitative, it is always possible to make the appropriate corrections after EDTA titration of carriers. Figures 1 and 2 show experimental elution curves for Hg(II) and Cd(II) deposited from 0.1M HNO_3 and 0.5M H_2SO_4 media. Fig. 1 was obtained by continuous detection and Fig. 2 by means of counting the collected fractions. The Hg(II) elution peak seems be better in the case of H_2SO_4 deposition. Table 5 shows total Hg retention on granulated copper.

Figure 3 shows part of the high resolution gamma spectrum for an irradiated powdered milk sample. After a quite long decay time the ^{203}Hg photopeak is clearly visible, and so are the ^{75}Se and other photopeaks. Table 6 shows some selected intensities for an irradiated pow-

Table 5: Hg(II) recovery in ashing - separation using granulated copper (Wet ashing: $\text{HClO}_4\text{-HNO}_3\text{-K}_2\text{Cr}_2\text{O}_7$).

SAMPLE	% Hg rec. in ashing	% Hg rec. in ashing + sepn.	% Hg.loss in ashing (*)
Powdered milk (200 mg)	89.7 91.2	89.2 91.2	10.3 8.8
chicken muscle (200 mg)	92.6	91.8	7.4

(*): Estimated by difference.

Table 6. Main isotopes found in irradiated powdered milk before and after radiochemical separation (on granulated copper columns).

ENERGY (KeV)	NUCLID	PEAK INTENSITY (total counts)	
		BEFORE	AFTER
136.0	^{75}Se	13308	6893
145.4	^{141}Ce	37234	N.D.
264.5	^{75}Se	8214	4213
279.2	^{203}Hg	6293	8506
487.0	^{140}La	1335	N.D.
496.3	^{131}Ba	11336	N.D.
602.7	^{124}Sb	12875	3677
1115.5	^{65}Zn	389442	1250
1596.2	^{140}La	667	N.D.
1691.0	^{124}Sb	3505	567

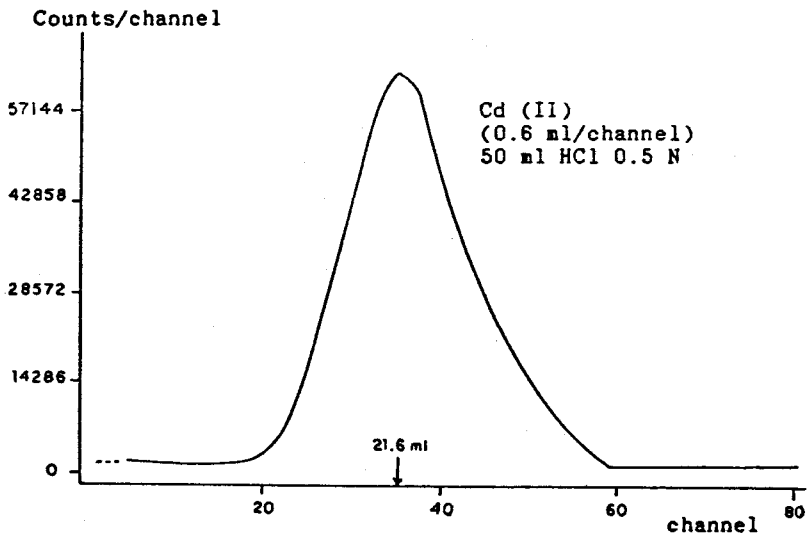
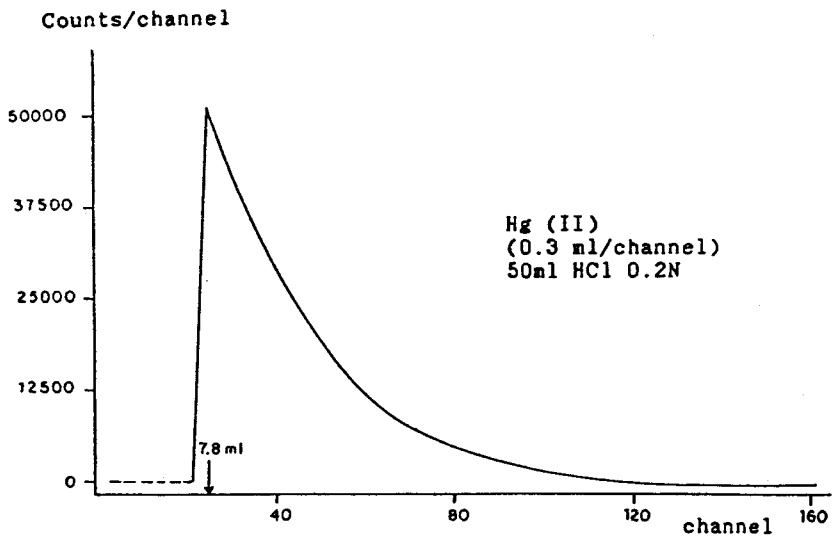


Fig. 1: Elution curves of Hg(II) and Cd(II) deposited from HNO₃ 0.1 M.

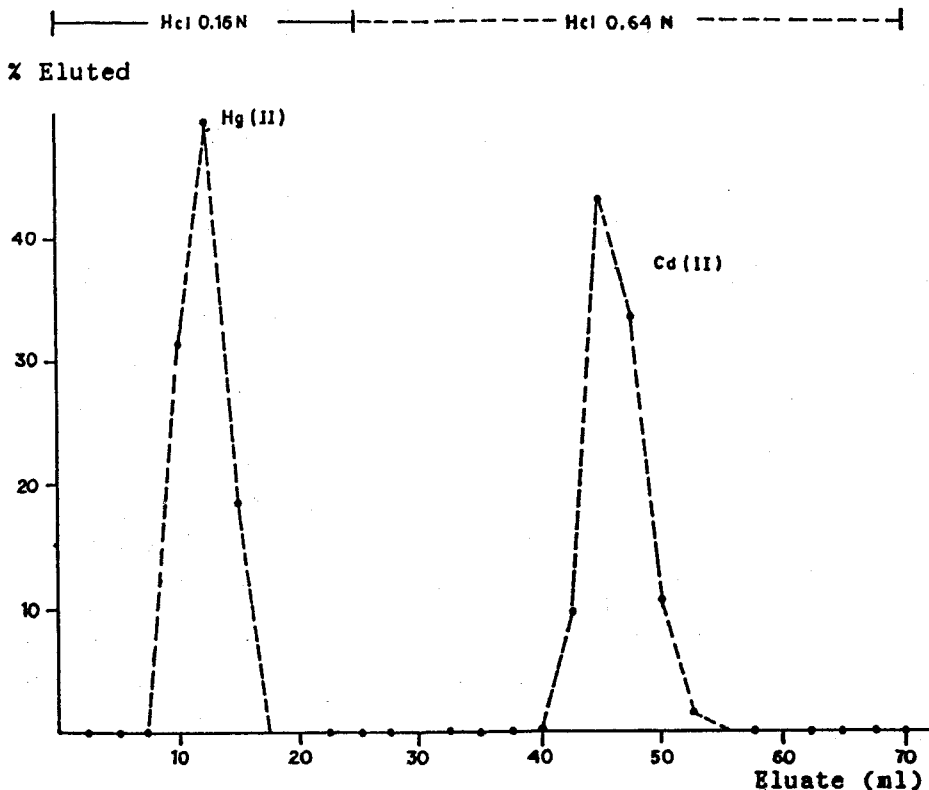


Fig. 2: Elution curves of Hg(II) and Cd(II) deposited from HNO₃ 0.5 M.

dered milk sample before wet ashing and for the granulated copper column after radiochemical separation. It was not possible to get a good separation of ²⁰³Hg from ⁷⁵Se.

The results allow us to think about the potential usefulness of cation exchange chromatography for Hg and Cd NAA. Anions are not retained and so ³²P, ⁸²Br, ⁷⁵Se are removed by passing the sample solution through the exchange column and washing with 0.5N H₂SO₄. Other cations such as ⁶⁴Cu and ⁶⁵Zn must be retained during Hg(II) and Cd(II) elution. ²⁴Na contamination of the Hg(II) and Cd(II) fractions may be a potential shortcoming. All the ²⁴Na could be removed during the 0.5N H₂SO₄ washing, by isotopic exchange selective elution, if the sulphuric solution contains some inactive Na₂SO₄. This will be explored in future experiments.

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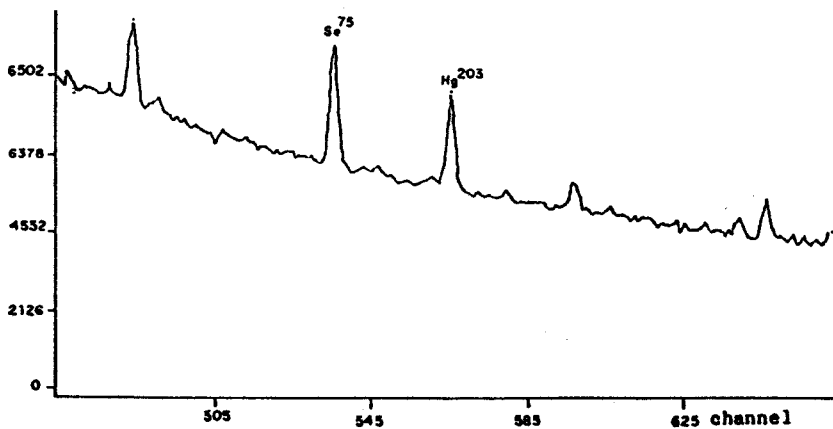
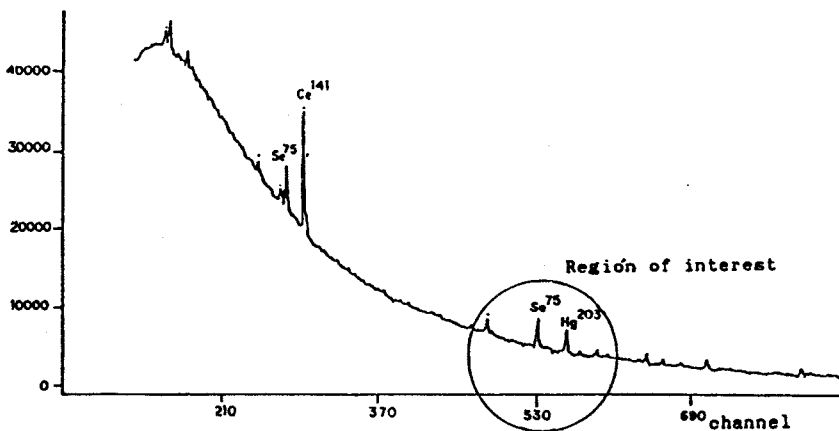


Fig. 3: (a) Gamma spectrum of an irradiated powdered milk sample (150 mg), after 2.5 months decay. (b) Amplified view of the region of interest.

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