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ABSTRACT

Fission products were determined in simulated high level radioactive waste solution by WDXRF without chemical separation.

Thin layer technique was employed for the sample preparation. The absorption effect verified for the L spectral lines was quantified and corrected accordingly.

The spectral interference was eliminated by the intensity ratio method. Overlapping correction of two interfering lines and sequential mode was applied to obtain desirable intensities. These results are compared with the data obtained by linear system of equations and free lines analysis.

Fission product analysis yielded a precision in the range of 0.1 to 5.0% and an accuracy of up to ± 8.0%. The results agree with those obtained by NAA and ICP techniques.

key phrases: x-ray analysis
fission product determination

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"DETERMINAÇÃO DOS PRODUTOS DE FISSÃO EM REJEITO LÍQUIDO DE ATIVIDADE ALTA POR FLUORESCÊNCIA DE RAIOS-X. CORREÇÃO DA INTERFERÊNCIA ESPECTRAL PELA RAZÃO DAS INTENSIDADES"

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RESUMO

Neste trabalho, os produtos de fissão Se, Rb, Y, Zr, Mo, Ru, Rh, Pd, Te, Cd, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu e Gd foram determinados diretamente numa solução simulada de rejeito radioativo de atividade alta por espectrometria de fluorescência de raios-X.

A técnica de deposição em camada fina foi empregada na preparação de amostras. O efeito de absorção, constatado para as radiações da série espectral L, foi quantificado e devidamente corrigido.

A interferência espectral foi eliminada pelo método de razão das intensidades. Uma superposição de 2 linhas interferentes e um modo sequential foi aplicado para obtenção das intensidades corrigidas. Foram averiguadas a influência da concentração do elemento interferente no valor da razão das intensidades e a eficiência do método. Os resultados são comparados com àqueles obtidos pelo sistema de equações lineares e pela medida das linhas livre de superposição.

A análise de produtos de fissão apresentou uma precisão de 0,1 a 5,0% e um desvio relativo de até 8,0%. Os resultados são concordantes com os da análise por ativação e espectrometria de emissão com fonte de plasma.

INTRODUCTION

The disposal of the high level radioactive waste is one of the crucial issues facing the nuclear industry and is generating serious debate. The generally accepted way is to incorporate the waste into a solid matrix, that is then placed in a deep geological repository.

Even though, many kinds of waste forms have been proposed, immobilization in borosilicate glass is considered to be the best suited process. However, great care has to be exercised to prevent the release of radionuclides into the environment from where it could reach human beings.

Much efforts are presently being made in developing adequate conditioning techniques that keep the waste immobilized. A knowledge of the chemical composition of the radioactive waste contributes largely to the sucess of such efforts. With this in mind, a simulated high level nuclear radiactive waste liquid of PWR reactor (IEA/TRS[1]) with 36,000 MWd/t burn-up was prepared. The liquid waste was prepared by the dissolution of oxides or nitrates of the same fission product elements in 5N nitric acid.

A suitable technique for fission product determination is x-ray spectrometry. This technique has successfully been applied to the analysis of the numerous materials, due to its multielemental character, high precision, accuracy and sensibility. Chemical separation is often unneccessary, because spectra of the individual elements can clearly be differentiated.

In this work the fission products, such as Se, Rb, Y, Zr, Mo, Ru, Rh, Pd, Te, Cd, Cs, Ba, La, Ce, Pr, Sm, Eu and Gd were determined by wavelength dispersive x-ray fluorescence. The spectral interference on the YKα, ZrKα, MoKα, LaLα, CeLα, PrLα, NdLα, SmLα lines was eliminated by the intensity ratio method.

EXPERIMENTAL

Sample Preparation

An aliquot of 50μℓ of solution was dried carefully by stream of air or low heating until 40°C onto a 20mm diameter on millipore filter. It is then placed between two foils of mylar sheet for preparation of thin layer samples.

The authors such as Brodda et al.[2] has been employed thin layer technique for radioactive sample preparation, mainly for effluent streams containing irradiated materials from reprocessing plants.

Matrix effects, such as primary and secondary x-ray absorption effect and inter-elemental excitation have to be considered in quantitative x-ray analysis. These effects however are reduced dratically by applying the thin layer technique. Another advantage is the utilization of small aliquot of sample, because large aliquots would result in a severe deterioration of the detection limit, due to increased scattering effect proceeding from the β and γ radiations of activity samples.

Five sets of standard aqueous solutions were prepared from specpure grade chemicals nitrate or oxide compounds. Triplicate samples were prepared for simulated high level waste and for each standard solutions. The relative instability of the filter samples associated with the slowly but significant radiolytical decomposition of nitrate to oxide under intensive x-ray irradiation, induce a bias in countings. Therefore internal deviation counting was not considered. Only single measurement was made for each sample and the average of fluorescent intensities of triplicate samples was used for calculations.

Spectral interference correction

Intensity ratio method for overlapping correction is usually used to correct single interfering line and is used in isolated form by authores such as Roelandts[3] and Rocca et al.[4]. For example, for the obtention of the corrected fluorescent intensity of YKα line that has RbKβ1 line interference, equation (1) was used:

$$YK\alpha_{corrected} = (YK\alpha + RbK\beta_1) - [RbK\beta_1(YK\alpha)/RbK\alpha]\ RbK\alpha \qquad (1)$$

were

$YK\alpha_{corrected}$ .... corrected fluorescent intensity of YKα line,

$(YK\alpha + RbK\beta_1)$ .... total fluorescent intensity measured in sample (intensity of YKα line plus intensity of interfering RbKβ1 line),

$[RbK\beta_1(YK\alpha)/RbK\alpha]$.... intensity ratio between RbKβ1, under YKα line, and RbKα lines determined in the Rb pure solution,

RbKα .... fluorescent intensity of RbKα line measured in sample.

For the fission product determination, a sequential mode was applied and two interfering lines were corrected to obtain desirable fluorescent intensities.

For example, the Figure 1 shows the way to obtain the corrected intensity of SmLα line. This line has two interfering lines: NdLβ1 and CeLβ2. For the determination of interfering fraction of NdLβ1 line, we have to know the corrected fluorescent intensity of NdLα. Otherwise, it is overlapped with CeLβ1 line. For the calculation of these interfering fraction, we need to know the corrected intensity of CeLα, which again is overlapped with BaLβ1 line. Finally the interfering fraction of BaLβ1, under CeLα line, is determined by

BaLα line, that is free of spectral interferences in the sample.

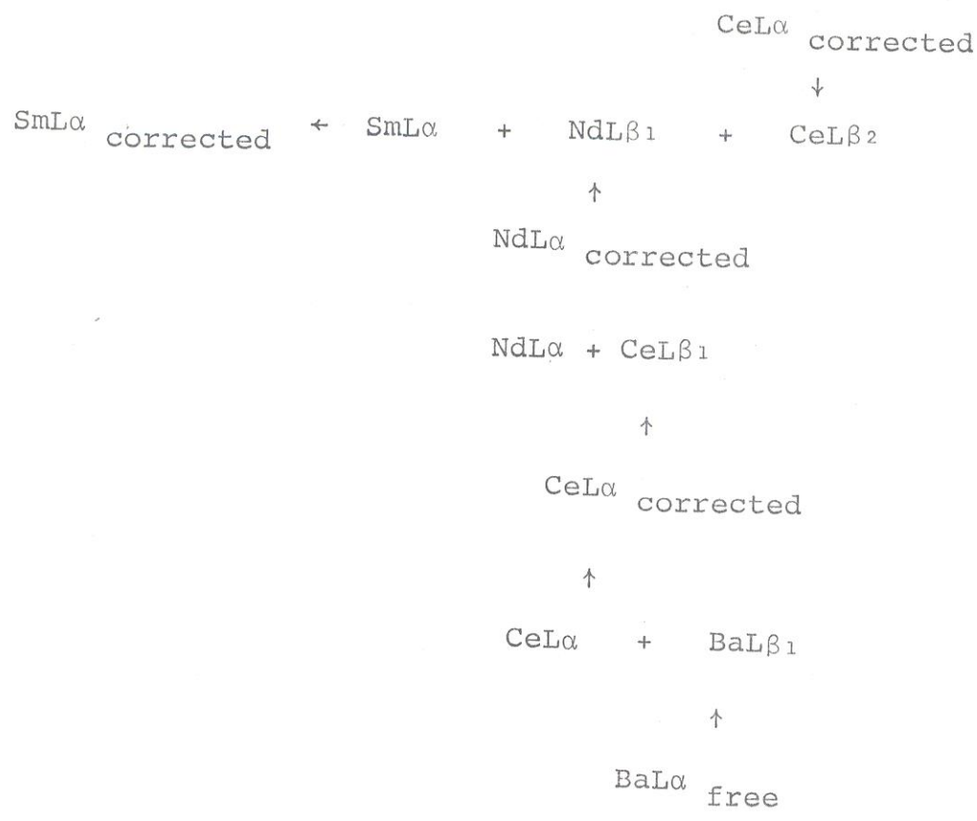

Figure 1. Sequential correction for obtention of corrected fluorescent intensity of SmLα line

In the Table 1 are listed the analytical lines to be measured, interfering lines and overlapping degree values determined experimentaly. Which shows different degrees of overlapping, since total overlapping such as for $RbK\beta_1(YK\alpha)/RbK\beta_1 = 1.007 \pm 0.0004$ to partial overlapping of less than 1% such as for $NdK\beta_1(SmL\alpha)/NdL\beta_1 = 0.0073 \pm 0.0002$.

Depending on the degree of overlapping, there is a concentration level of interfering element which does not cause spectral interference in analyte line due to the peak broadening. Therefore while using intensity ratio method for spectral interference correction has to be taken care about the utilization of values of intensity ratio, that were determined mainly in the experimental form.

TABLE 1 - Spectral interference and overlapping degree for different analysing crystal

ELEMENT	ANALYTICAL TO BE MEASURED (nm)	LINE INTERFERING (nm)	OVERLAPPING DEGREE	ANALYSING CRYSTAL
Y	YKα (0.0829)	RbKβ1 (0.0829)	RbKβ1 (YKα)/RbKβ1 = 1.007 ± 0.0004	LiF(220)
Zr	ZrKα (0.0786)	SrKβ1 (0.0783)	SrKβ1 (ZrKα)/SrKβ1 = 0.354 ± 0.004	LiF(220)
Mo	MoKα (0.0709)	ZrKβ1 (0.0702)	ZrKβ1 (MoKα)/ZrKβ1 = 0.0189 ± 0.0003	LiF(220)
La	LaLα (0.2666)	CsLβ1 (0.2683)	CsLβ1 (LaLα)/CsLβ1 = 0.0589 ± 0.005	PET(002)
Ce	CeLα (0.2561)	BaLβ1 (0.2568)	BaLβ1 (CeLα)/BaLβ1 = 0.66 ± 0.01	PET(002)
Pr	PrLα (0.2463)	LaLβ1 (0.2459)	LaLβ1 (PrLα)/LaLβ1 = 0.831 ± 0.004	PET(002)
Nd	NdLα (0.2370)	CeLβ1 (0.2356)	CeLβ1 (NdLα)/CeLβ1 = 0.182 ± 0.003	PET(002)
Sm	SmLα (0.2199)	CeLβ2 (0.2209)	CeLβ2 (SmLα)/CeLβ2 = 0.411 ± 0.001	PET(002)
		NdLβ1 (0.2167)	NdLβ1 (SmLα)/NdLβ1 = 0.0073 ± 0.0002	PET(002)
Eu	EuLα (0.2121)	NdLβ3 (0.2126)	NdLβ3 (EuLα)/NdLβ3 = 0.547 ± 0.001	Ge (111)
		PrLβ2 (0.2119)	PrLβ2 (EuLα)/PrLβ2 = 0.913 ± 0.005	Ge (111)
Gd	GdLα (0.2047)	NdLβ2 (0.2035)	NdLβ2 (GdLα)/NdLβ2 = 0.231 ± 0.006	Ge (111)
		LaLγ2 (0.2046)	LaLγ2 (GdLα)/LaLγ2 = 1.04 ± 0.01	Ge (111)
		CeLγ1 (0.2048)	CeLγ1 (GdLα)/CeLγ1 = 0.965 ± 0.001	Ge (111)

The values of intensity ratios listed in the Table 2 were determined separatelly from pure solutions of elements, with concentrations similar to the high level radiactive liquid sample. The use of these values is correct for a small range of interfering element concentration with a variation of at least 10 times. The use of uncorrected values of intensity ratio lead to systematic errors producing inaccurate results.

The efficiency of intensity ratio method was ivestigated. For that binary system Y-Rb was prepared. The yttrium concentration was fixed at 1.2 g ℓ^{-1} and rubdium concentration was varied from 1.0 to 5.0 g ℓ^{-1}. The corrected intensity of YKα line was obtained by equation (1). The Table 3 shows the average of corrected intensity of YKα line was 1377 ± 16 counts s^{-1}. The sample containing only yttrium (1.2 g ℓ^{-1}) gave a counting of 1395 ± 14 counts s^{-1}. Moreover the straight line equation of (YKα + RbKβ_1) intensity is A = (1375 ± 17) + (80 ± 5)B, where the values of intercept, that means yttrium concentration is 1.2 g ℓ^{-1} is 1375 ± 17 counts s^{-1}.

The data show the efficiency of intensity ratio method indicading that any residual or systematic error affect the obtention of corrected intensities, when corrected intensity ratio values are used.

This kind of assay was extended for binary system such as Zr-Sr, Pr-La and Nd-Ce. All systems showed the same efficiency for spectral interference correction.

TABLE 2 - Experimental intensity ratio values

ELEMENT	CONCENTRATION ($g\ \ell^{-1}$)	INTENSITY RATIO	ANALYSING CRYSTAL
Rb	1.0	$RbK\beta_1$ (YKα)/RbKα = 0.2281 ± 0.0005	LiF(220)
Sr	2.0	$SrK\beta_1$ (ZrKα)/SrKα = 0.0823 ± 0.0007	LiF(220)
Zr	9.0	$ZrK\beta_1$ (MoKα)/ZrKα = 0.00451 ± 0.00006	LiF(220)
Cs	6.0	$CsL\beta_1$ (LaLα)/CsLα = 0.0353 ± 0.0003	PET(002)
Ba	4.0	$BaL\beta_1$ (CeLα)/BaLα = 0.079 ± 0.001	PET(002)
La	3.0	$LaL\beta_1$ (PrLα)/LaLα = 0.479 ± 0.002	PET(002)
		$LaL\gamma_2$ (GdLα)/LaLα = 0.0176 ± 0.0007	Ge (111)
Ce	6.0	$CeL\beta_1$ (NdLα)/CeLα = 0.052 ± 0.002	PET(002)
		$CeL\beta_2$ (SmLα)/CeLα = 0.091 ± 0.001	PET(002)
		$CeL\gamma_1$ (GdLα)/CeLα = 0.077 ± 0.006	Ge (111)
Pr	3.0	$PrL\beta_2$ (EuLα)/PrLα = 0.1410 ± 0.0006	Ge (111)
Nd	9.0	$NdL\beta_1$ (SmLα)/NdLα = 0.0047 ± 0.002	PET(002)
		$NdL\beta_3$ (EuLα)/NdLα = 0.04919 ± 0.0006	Ge (111)
		$NdL\beta_2$ (GdLα)/NdLα = 0.037 ± 0.001	Ge (111)

TABLE 3 - Verification of the efficiency of intensity ratio method for spectral interference correction System Y-Rb : YKα and RbKβ1 lines overlapping

[Y] ($g\ \ell^{-1}$)	[Rb] ($g\ \ell^{-1}$)	YKα + RbKβ1 MEASURED (counts s^{-1})	RbKα MEASURED (counts s^{-1})	[Rbβ1(YKα)] CALCULETED (counts s^{-1})	YKα CORRECTED (counts s^{-1})
1.20	0.0	1395 ± 14	...	...	...
1.20	1.0	1458 ± 15	260 ± 6	70 ± 3	1387 ± 14
1.20	2.0	1540 ± 16	599 ± 9	151 ± 5	1389 ± 14
1.20	3.0	1592 ± 15	880 ± 11	237 ± 6	1354 ± 14
1.20	4.0	1709 ± 16	1191 ± 13	321 ± 7	1388 ± 14
1.20	5.0	1771 ± 16	1501 ± 15	405 ± 8	1365 ± 14

A = (1375 ± 17)
(80 ± 5)

Average: 1377 ± 16

Matrix Effect

The absorption effect and/or inter-elemental excitation caused by matrix are drastically reduced by the utilization of thin layer technique for sample preparation.

However Eddy and et al.[6] observed absorption effects in thin layer samples during the determination of the elements W and Mo. They verified the absorption effect on WLα line with the increase of mass deposit on filter paper. For MoKα line, they did not find any significant absorption effect. These authors used the internal standard method for correction of absorption effect on WLα line.

In the present paper, the Rasberry-Heinrich, Lucas Tooth-Pyne and Lachance-Trail relations[7], which are generally used to investigate matrix effect in metallic samples, were applied to investigate this effect on filter millipore. In the present study, binary system such as Sr-Cs, Cs-Sr and Ce-Sr were prepared and followings relations were applied:

1. Straight line: I_i vs C_j

2. Rasberry-Heinrich: C_i/I_i vs $C_j/(1 + C_i)$

3. Lucas Tooth-Pyne: C_i/I_i vs I_j

4. Lachance-Trail: C_i/I_i vs C_j

were

I_i, C_i .... intensity and concentration of element i,

I_j, C_j .... intensity and concentration of interfering elemen j.

In Figure 2, all the four relations show significant absorption effect on CeLα line with the increase of Sr concentration or mass loaded on filter millipore. But for the spectral serie K no

absorption effect was verified, where the intensity of SrKα line did not show any effective absorption effect with the increase of Cs concentration as it is shown in Figure 3.

The difference of mass absorption coefficient between standard and waste solution was corrected by following equation[5], where the same amount of element was added in two different matrices.

$$\frac{I_1 M_1}{I_2 M_2} = \frac{\mu(\bar{\lambda}) M_2}{\mu(\bar{\lambda}) M_1} = f$$

where:

I_1, $\mu(\bar{\lambda})M_1$ .... intensity of element i and mass absorption coefficent of matrix M_1 for the weighted average wavelength $\bar{\lambda}$,

I_2, $\mu(\bar{\lambda})M_2$ .... intensity of element i and mass absorption coefficient of matrix M_2 for the weighted average wavelength $\bar{\lambda}$.

The constant f was determined experimentally by addition of exact known quantities of Cs, La, Ce and Pr elements in standard and waste sample solutions.

The elements Cd, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu and Gd whose determination were realized by measurement of L lines, in the end of theirs determination the absorption effect was corrected accordingly using experimental value of $f = 1.26 \pm 0.02$.

Apparatus

The sequential spectrometers of Siemens model SR-1 and of Rigaku Denki model 4053A3 were used for fluorescent intensities measurements. A scintilation or gas flow counter with vacuum or

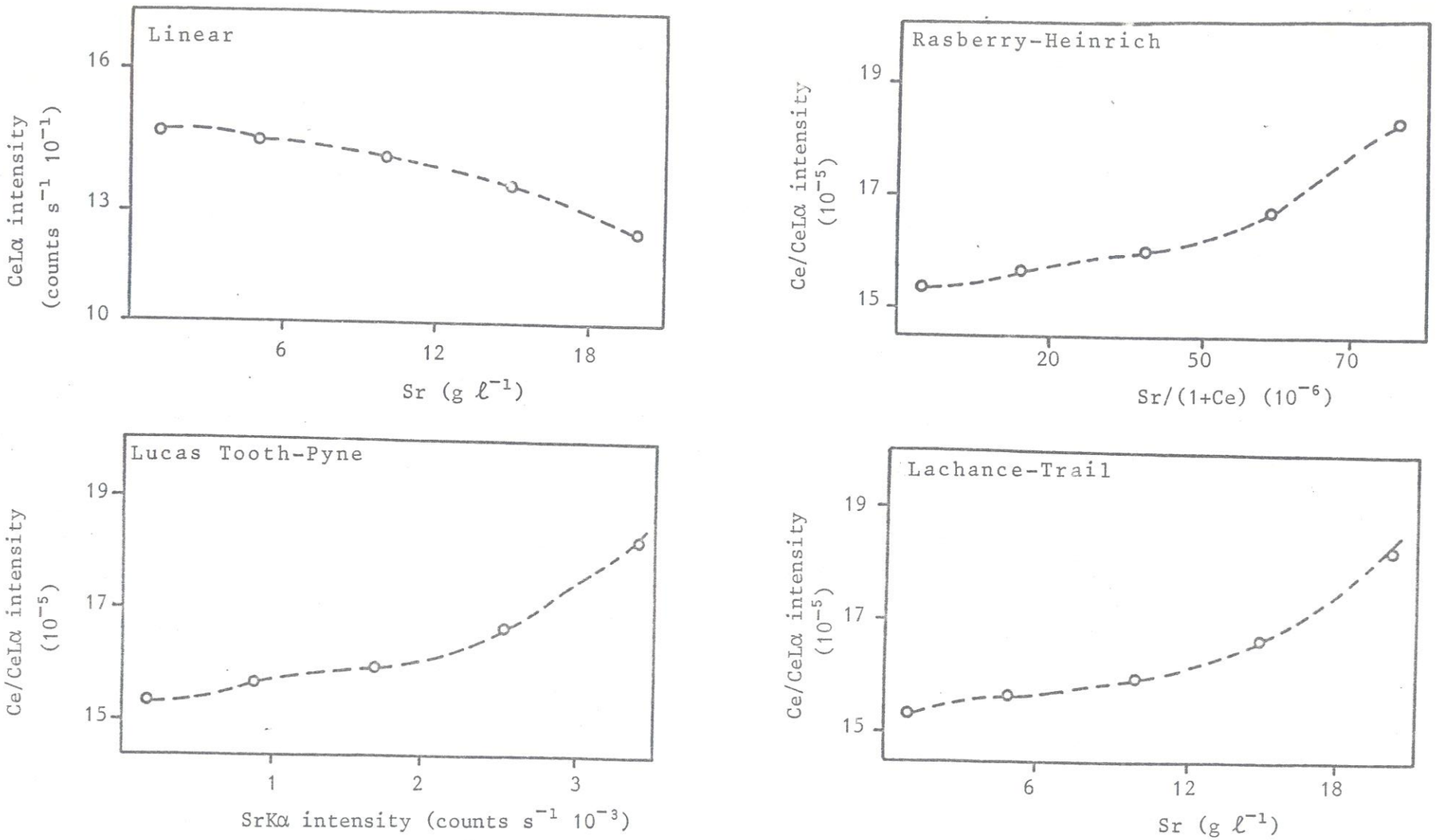

FIGURE 2: Verify of matrix effect for Ce-Sr system

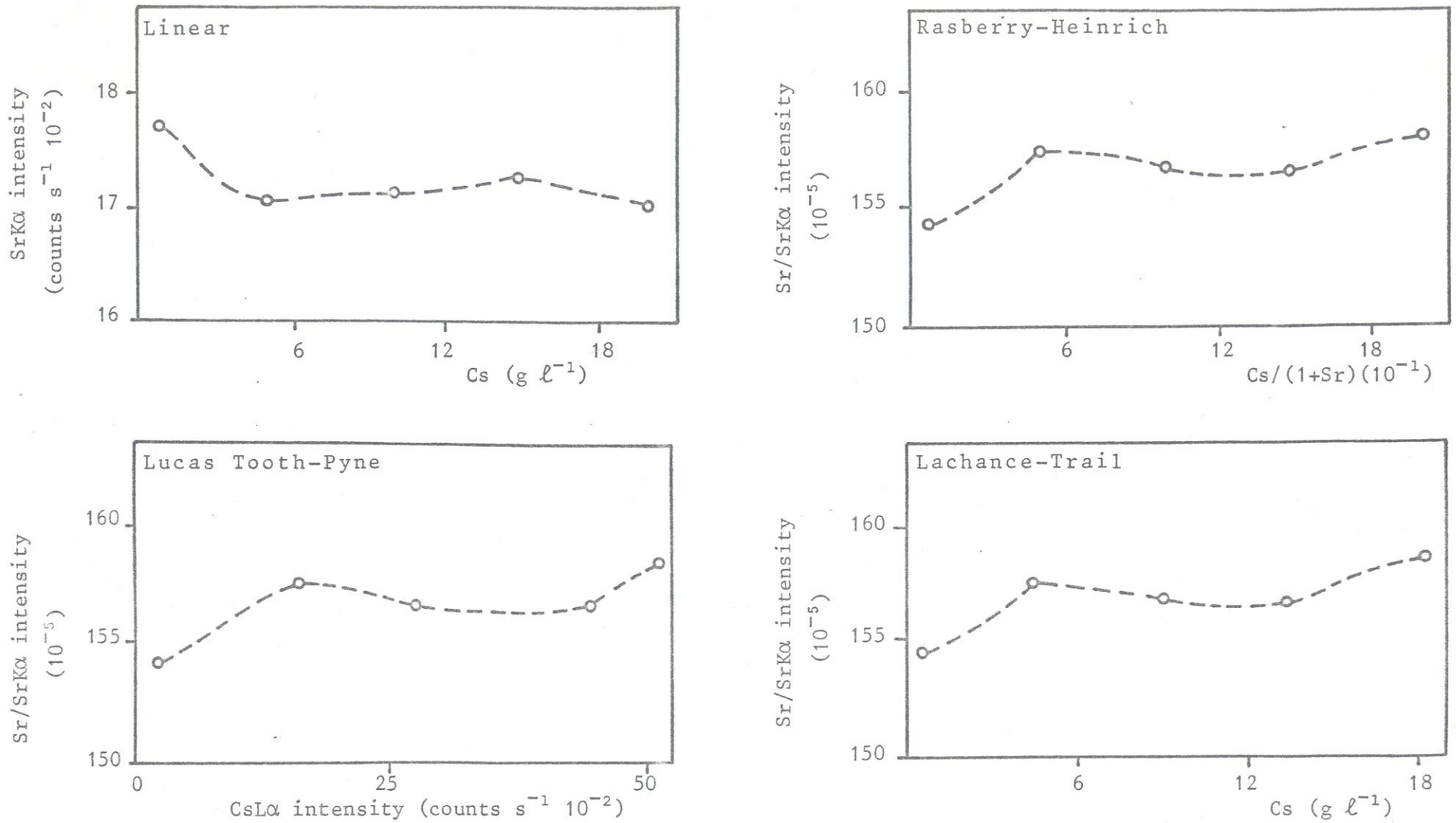

FIGURE 3: Verify of matrix effect for Sr-Cs system

helium atmosphere were used depending on the radiation to be measured.

Linear System of Equations Method and Free Lines Analysis

The elements Cs, Ba, La, Ce, Pr, Nd and Sm were determined by linear system of equations method described elsewhere[8].

The spectral interference free lines such as $CsL\beta_3$, $PrL\beta_1$, $NdL\beta_1$, $SmL\beta_1$, $EuL\beta_1$ and $GdL\beta_1$ were measured to determine corresponding elements.

These results ofter an additional data to compare the data obtained by intensity ratio method.

Calibration Curves

For each standard solution triplicate sample were prepared and net fluorescent intensities were obtained. The lines $YK\alpha$, $ZrK\alpha$, $MoK\alpha$, $LaL\alpha$, $CeL\alpha$, $PrL\alpha$, $NdL\alpha$ and $SmL\alpha$ were corrected using a corresponding equation (1) and when necessary for the obtention of corrected fluorescent intensities sequential mode was applied.

In Table 4 are listed, as an example, the data of concentration of elements and the measured and corrected intensities for construction of La and Pr calibration curves. The data for these curves are listed below.

	Straight line equation (Y=a+bx)		Standard	Correlation
Element	$a \pm s_a$	$b \pm s_b$	Deviation	Coefficient
La	0	156.4 ± 0.1	±12	0.999
Pr	-15 ± 1	73 ± 1	± 6	0.997

TABLE 4 - Data for La and Pr calibration curves

SAMPLE	CONCENTRATION ($g\ \ell^{-1}$)			MEASURED INTENSITIES (counts s^{-1})			CORRECTED INTENSITIES (counts s^{-1})	
Nº	Cs	La	Pr	CsLα	LaLα + CsLβ1	PrLα + LaLβ1	LaLα	PrLα
St 1	10.0	1.0	5.0	6573	369	419	137	353
				7143	405	424	153	351
				6563	373	432	141	364
St 2	8.0	2.0	4.0	5269	486	407	300	263
				5398	504	424	313	274
				5214	486	416	302	271
St 3	6.0	3.0	3.0	4008	622	433	481	203
				3998	618	427	477	201
				4046	617	435	474	208
St 4	4.0	4.0	2.0	2590	721	430	630	128
				2596	717	431	625	132
				2547	709	431	619	134
St 5	2.0	5.0	1.0	1294	810	425	764	59
				1331	829	435	782	60
				1379	853	445	804	60
Sample				3364	483	365	408	170
				3390	471	357	407	162
				3329	474	356	396	166

Equations used: $LaL\alpha_{corrected} = (LaL\alpha + CsL\beta_1) - [CsL\beta_1\ (LaL\alpha)/CsL\alpha]\ CsL\alpha_{free}$

$PrL\alpha_{corrected} = (PrL\alpha + LaL\beta_1) - [LaL\beta_1\ (PrL\alpha)/LaL\alpha]\ LaL\alpha_{corrected}$

The two curves presented a good correlation coefficient and within significant level 0.95, the intercept of La calibration curve can be considered to be zero estatistically.

The fission product determination were outlined by construction of corresponding curve for each element.

RESULT AND DISCUSSION

In x-ray fluorescence analysis, many authors, such as Ryabuklin et al.[9] and Galson et al.[10] have investigated experimental methods for spectral interference correction. These authors have used different experimental conditions, employing high resolution crystal analysers and utilizing second order reflection line. This practise usually lead to loss in fluorescent intensity to be measured and the increase of couting time, thereby increase in the cost of analysis.

In the present work, the spectral interference was corrected by intensity ratio and linear system of equations methods. In the Table 5, are listed the analysis of fission products in simulated high level radioactive waste, where they were determined by a combination of three different methods: intensity ratio, linear system of equations and free line analysis.

X-ray fluorescence analysis has been known as a technique of high precision. For the three methods employed to determine fission products, the mass loaded on millipore filter varied aproximately from 2 $\mu g\ g^{-1}cm^{-2}$ for cadmium to 80 $\mu g\ g^{-1}cm^{-2}$ for Nd, whereas the precision of the results obtained varied from 0.4% for Rh ($0.980 \pm 0.004\ g\ \ell^{-1}$) to 9.0% for Cs ($5.53 \pm 0.05\ g\ \ell^{-1}$). In general, it can be observed that the same precision was achieved for intensity ratio method and free line analysis. However the precision obtained by linear system of equations method was much lower.

TABLE 5 - Results of fission product determination by WDXRF

		CONCENTRATION ($g\ \ell^{-1}$)		
		Intensity ratio method	Linear of system equations method	Free line analysis
ELEMENT	ADDICIONED	FOUND	FOUND	FOUND
Se	0.134	...	...	0.280 ± 0.007
Rb	0.87	...	...	0.846 ± 0.002
Sr	2.12	...	...	1.94 ± 0.005
Y	1.19	1.20 ± 0.01	...	...
Zr	9.33	9.10 ± 0.08	...	...
Mo	8.81	8.9 ± 0.1	...	...
Ru	5.49	...	...	5.402 ± 0.008
Rh	0.96	...	...	0.980 ± 0.004
Pd	3.6	...	...	3.71 ± 0.08
Te	1.42	...	...	1.37 ± 0.04
Cd	0.22	...	...	0.24 ± 0.02
Cs	6.18	6.30 ± 0.07	5.53 ± 0.05	6.03 ± 0.06
Ba	4.2	1.51 ± 0.08	0.38 ± 0.06	...
La	3.22	3.24 ± 0.05	3.2 ± 0.2	...
Ce	6.3	6.6 ± 0.3	5.58 ± 0.05	...
Pr	3.03	3.12 ± 0.05	2.03 ± 0.06	2.97 ± 0.03
Nd	10.5	11.0 ± 0.1	9.8 ± 0.1	9.9 ± 0.1
Sm	2.23	2.38 ± 0.03	1.89 ± 0.04	2.20 ± 0.04
Eu	0.45	...	...	0.48 ± 0.01
Gd	0.34	...	...	0.35 ± 0.01

In terms of accuracy, the intensity ratio method applied for the obtention of corrected YKα, ZrKα, MoKα, LaLα, CeLα, PrKα, NdLα and SmLα lines showed better results than linear system of equations method. The earlier method yielded relative error varying from -2.5% for Zr to 6.7% for Sm determination, where original and determined composition respectively are:

Zr : 9.33 g ℓ^{-1} vs 8.9 ± 0.1 g ℓ^{-1}

Sm : 2.23 g ℓ^{-1} vs 2.38 ± 0.03 g ℓ^{-1}

By the linear system of equations method only La and Pr determinations showed good results, where the relative error varied from -33.0% for Pr to -6.2% for La determination.

For spectral interference correction by intensity ratio method, the overlapping values were determined experimentally, using a pure solution of elements in a concentration similar to waste sample. This procedure was adequate because no systematic error was observed in the fission products determination. The use of uncorrected intensity ratio values can lead to inaccurate results.

The corrected fluorescent intensities of PrLα, NdLα and SmLα lines were obtained by combination of intensity ratio method plus sequential mode according to A and B shemes shown below. In the scheme A the obtention of suitable fluorescent intensities of PrLα line is explained; where it was necessary to introduce two sequential steps. The first step envolves the accounting of fractional interfering of CsLβ1 line and second envolves the calculation of the fractional interfering of LaLβ1 line. For obtention of corrected fluorescent intensities of NdLα two sequential steps are necessary and for SmLα line it is necessary to introduce four sequential steps to account for the fractional interference of BaLβ1, CeLβ1, NdLβ1

and $CeL\beta_2$ lines as shown scheme B.

Scheme A

$CsL\alpha$ free
↓
$CsL\beta_1$ interfering
↓
$LaL\alpha$ corrected
↓
$LaL\beta_1$ interfering
↓
$PrL\alpha$ corrected

Scheme B

$BaL\alpha$ free
↓
$BaL\beta_1$ interfering
↓
$CeL\alpha$ corrected

$CeL\beta_1$ interfering
↓
$NdL\alpha$ corrected
↓
$NdL\beta_1$ interfering

$CeL\beta_2$ interfering
↓
$SmL\alpha$ corrected

Even though larger statistical deviations in the countings was observed on correction of $SmL\alpha$ line than $NdL\alpha$ and $PrL\alpha$ lines, all the three determinations presented good precision and accuracy in the final results of analysis.

Eu and Gd were determined only by free lines analysis by the measurement of $EuL\beta_1$ and $GdL\beta_1$ lines respectively. $EuL\alpha$ lines has $NdL\beta_3$ and $PrL\beta_2$ interfering lines and $GdL\alpha$ has $NdL\beta_2$, $LaL\gamma_2$ and $CeL\gamma_1$ interfering lines. During the application of intensity ratio method for spectral interference on $EuL\alpha$ and $GdL\alpha$ lines were presented a great deviation in the countings. Under same experimental conditions the measurement of weak analytical line and low concentration of elements in sample contribute to greater imprecision in the results of x-ray fluorescence analysis. Therefore Eu and Gd elements, whose concentration on millipore filter were around 3 $\mu g\ g^{-1}cm^{-2}$, associated with the introduction of intensity ratio method and sequential mode for correction of interfering lines, lead to a great statistical deviations in the countings, becoming their determination impossible. But it can be noticed that for elements whose concentration is above

1.0 g ℓ^{-1}, that means the mass loaded on millipore filter is above 6 μg $g^{-1}cm^{-2}$, the correction of two or more interfering lines becomes possible, because the statistical deviations can be overcome.

Following the same criteria, the Cd, whose concentration on millipore filter is less than 2 μg $g^{-1}cm^{-2}$ and the concentration of its calibration curve varied from 0.4 to 3 μg $g^{-1}cm^{-2}$ presented an higher imprecision than determination of other elements by free lines analysis. By WDXRF analysis the determination of elements whose concentration is lower than 0.2 g ℓ^{-1} better experimental conditions need to be established or chemical separation or preconcentration techniques have to be applied for its determination.

In general, the intensity ratio method presented better precision and accuracy than linear system of equations method for spectral interference correction, in spite of more correction stage such as intensity ratio values and sequential mode were introduced to obtain suitable fluorescent intensities.

The experimental correction used for different absorption effect between standard and waste sample solution showed to be adequate, because the results of analysis did not show any systematic error. For application of the same kind of correction between unknown sample and standard, it is necessary to add the elements with same order of x-ray emission energy, so that the energy of radiation has the same influence in two different matrices.

The results of analysis by WDXRF, NAA and ICP techniques are listed in Table 6. Selenium concentration is 0.280 ± 0.007 and 0.211 ± 0.002 g ℓ^{-1} when it is analysed by WDXRF and NAA techniques. This value does not agree with original composition, indicating a probable error in sample preparation. Barium is slowly and constantely precipeted in high HNO_3 solution due to its slow solubility, therefore its concentration is different from of original solution.

TABLE 6 - Comparison of WDXRF, NAA and ICP techniques for fission product determination

ELEMENT	WDXRF CONCENTRATION g ℓ^{-1}	WDXRF RELATIVE ERROR (%)	NAA CONCENTRATION g ℓ^{-1}	NAA RELATIVE ERROR (%)	ICP CONCENTRATION g ℓ^{-1}	ICP RELATIVE ERROR (%)
Se	0.280 ± 0.007	+ 108.9	0.211 ± 0.002	+ 57.5	.....	
Y	1.20 ± 0.01	+ 0.8	.....		1.23	+ 3.4
Mo	8.9 ± 0.1	+ 1.0	8.4 ± 0.6	- 4.6	.....	
Cs	6.30 ± 0.07	+ 1.9	7.7 ± 0.1	+ 24.6	.....	
La	3.24 ± 0.05	+ 0.6	3.64 ± 0.08	+ 13.4	3.48	+ 8.1
Ce	6.6 ± 0.3	+ 4.8	5.5 ± 0.2	- 12.7	.....	
Pr	3.12 ± 0.05	+ 3.0	3.42 ± 0.01	+ 13.2	3.63	+ 19.8
Nd	11.0 ± 0.1	+ 4.8	9.8 ± 0.2	- 6.7	11.80	+ 12.4
Sm	2.38 ± 0.03	+ 0.7	2.47 ± 0.07	+ 10.8	2.31	+ 3.6
Eu	0.48 ± 0.01	+ 6.7	0.48 ± 0.02	+ 6.7	0.51	+ 13.3
Gd	0.35 ± 0.01	+ 2.9	0.343 ± 0.004	+ 0.9	1.04	+205.9

Cs determination by NAA technique and Pr and Gd analysis by ICP technique show some matrix effect in their determination, where they presented considerable relative error, of the order of +19.8 to +205.9% in the values. In general, WDXRF technique showed the same or better efficiency than the NAA and ICP techniques in fission product determination. Moreover, the WDXRF analysis showed to be better than other techniques in its capacity to analyse greater number of elements demonstrating its powerful capacity for multielemental analysis. Also, the method has the advantage to easy sample preparation, where hot samples can be prepared fully by remote control and requering only few aliquots for sample preparation, around 50 μℓ. Therefore the personal safety is assured by maintenance of radiation level within the permissible dose.

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