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## **SEPARATAS**

**A NEW INSTRUMENTAL METHOD FOR THE ANALYSIS OF RARE EARTH ELEMENTS**

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## **A New Instrumental Method for the Analysis of Rare Earth Elements\***

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### **Abstract**

A method for the simultaneous elemental analysis of the Rare Earths is proposed and empirically verified. It is based on the analysis of the escape peaks, generated by the characteristic X-Rays of these elements in a Xenon Proportional Counter. The peaks are well resolved and intense, in contrast to the photopeak which is lost in the background.

The spectra are generated by a radioisotope such as  $\text{Co}^{57}$ , and the equipment is simple, portable and low cost, although resolution challenges that of the best solid state detectors.

Since X-rays are utilized, matrix, granulometric or mineralogical effects are minimal, and the method is rapid, sensitive, non-destructive and requires little or no sample preparation. The results are preliminary and an improvement in resolution of up to fourfold seems possible; precision is better than 0,1% in concentrated samples and sensitivity is about 20  $\mu\text{g}$ .

\* Based on part of a Free-Docency Thesis work conducted at the Chemistry Dept. of the Instituto de Ciências Exatas da Universidade Federal de Minas Gerais.

## I - INTRODUCTION

The elemental analysis of the Rare Earth Elements (REE) is a complex and difficult problem, given their great similarity in chemical, physico-chemical and nuclear properties<sup>(1,2,3)</sup>. Chemical methods (ion-exchange chromatography, recrystallization, etc.) are complex and tedious. Atomic methods (atomic absorption, atomic emission, X-Ray spectrometry, etc.) are either limited or demand complex and expensive instruments or sample preparation techniques and are very subject to interference. Nuclear Activation Methods, besides requiring access to a nuclear reactor, is of complex interpretation and subject to interference, besides normally requiring chemical separation since the spectra are complex and very similar.

The method developed in this work has several advantages over more conventional ones, to wit: it is non-destructive and capable of the simultaneous analysis of all the REE; it is little subject to interference, and relatively free of matrix, mineralogical, granulometric, sample preparation or solvent effects. It is instrumental, low cost, rapid, simple to interpret and to implement in routine and requires little or no maintenance, such as gases, refrigerants, etc. The equipment is compact and rugged being ideal to industrial or field uses, such as on-line monitoring, since it is remote sensing and results are accessible almost immediately. The only comparable technique is fluorescence analysis with a small area Ge/Li detector of very high resolution, which is difficult to implement due to the high cost and fragility of the equipment; the requiring of frequent maintenance and supply of liquid Nitrogen, and the much smaller sensitivity.

## II - DESCRIPTION OF THE METHOD

The method is based on the detection of the K X-Rays of the REE excited by radioisotopes or X-Ray tubes. It is similar to the conventional X-Ray fluorescence analysis excited by radioisotopes, but it differs essentially in the method of detection of these characteristic X-Rays. In the conventional method the selectivity is obtained via K-edge filters<sup>(4)</sup>, the use of high-resolution counters such as solid-state detectors<sup>(5)</sup> or, as in the X-Ray Spectrometer, by means of Bragg Diffraction in a Crystal<sup>(6)</sup>.

More usual detectors, such as Scintillators and Proportional Counters lack the resolution to separate neighbouring elements. K-edge filtering utilizing the Ross filter technique is capable of analysing only one element at a time and is imprecise and insensitive, since the result is the difference of two large and proximate numbers. The conventional X-Ray Spectrometer is an expensive and complex instrument, and is limited to the analysis of the LX-Rays for the REE, since the Bragg angle for the KX-Rays of the REE is below its capability. Due to this, and given the low penetrating power of the LX-Rays and the fact that their spectra is considerably more complicated than the KX-Ray Spectrum, this analysis is very subject to interferences arising from matrix and sample preparation effects, among others.

In the method, object of the present work, the detection of the K-X-Rays of the REE is done with a Xenon Proportional Counter, with the essential difference that the Escape X-Rays are observed. With this, the resolution is much improved over that obtainable for the full absorption peaks.

Besides, the detection of full absorption peak would require a very high pressure in the counter, to avoid the loss of resolution resulting from wall effects<sup>(7)</sup>, but such a counter requires an exceedingly high voltage and is of poor performance and impractical.

In the usual case of detection by a proportional counter the photon impinges in an atom of the gas and extracts the K electron, the cross section for other effects such as higher orbit photoeffects, Compton and Rayleigh scattering, etc, being negligible. The photoelectron has a kinetic energy of  $E = E_i - E_{k0}$ , where  $E_i$  is the incident photon energy and  $E_{k0}$  the extraction energy of the K electron of the detecting gas. This photoelectron then causes ionizations in the gas and the number of ions formed is proportional to its kinetic energy. These ions are multiplied by an avalanche process and generate a current pulse in the anode, of a value proportional to the photoelectron energy E. The excited gas atom releases its energy by generating a cascade of K, L, M, N, etc. X-Rays, until it returns to the ground state. For Xenon, the Auger electron contribution is negligible at the energy of the REE K X-Rays, given that the K fluorescence yield is larger than 95%, but it is considerably larger for lighter gases<sup>(8)</sup>.

In a typical Xenon Proportional Counter, the detection efficiency for the energetic Xenon K X-Rays is small, since the cross-section has a pronounced minimum at this characteristic energy, and the density is relatively little, with the result that the escape probability is large. For the other L, M, N, etc, X-Rays in the cascade which have a much lower energy, the situation is reversed and absorption is practically total. When the K X-Ray of Xenon, generated in the photodetection process, is reabsorbed in the gas together with the rest of the cascade, the generated signal corresponds to the full incident energy and gives the photopeak (or full energy peak) in the spectrum. If the K-X ray escapes, the signal detected is proportional to  $E_i - E_k$  where  $E_k$  is the energy of the K-X Ray of Xenon.

By varying pressure and diameter of the counter, conditions can be optimized for the detection of the escape X-rays and for the REE and a Xenon counter the optimum for a 2" diameter tube occurs at around 1 to 2 atmospheres, the usual filling pressure. The detection efficiency for escape X-Rays is given approximately by:

$$\eta = (1 - e^{-\mu_0 x})e^{-\mu_1 x}$$

where the first term gives the probability of detection of the incident X-Ray and the second one that of escape of the Xenon K X-Ray. Here  $\mu_0$  and  $\mu_1$  are the cross-sections and x the thickness of the detecting gas. The resulting curve is displayed in Fig. 1 and shows a broad maximum. Furthermore, the intrinsic detection efficiency is high, being around 40% for this situation, with consequent good

sensitivity of analysis. By comparison, the full energy intrinsic detection efficiency is only around about 3%.

The resolution of Proportional Counters is given approximately by  $R = 0.40\sqrt{E}$ , where  $R$  and  $E$  are in KeV<sup>(9)</sup>, and  $E$  is the energy dissipated in the gas. For the REE the K X-Ray energy varies from 33 to 54 KeV where the resolution of Proportional Counters is about 8%, while the energy separation between adjacent REE is only about 4%. These counters are, thus, incapable of resolving these elements.

For the escape peaks, however, the resolution, by the formula above, becomes:

$$R = 0.40 \sqrt{E_i - E_k}$$

amounting to only 1% to 3% as the incident energy ranges from Lanthanium to Lutetium, and since the energy separation is the same as above, the resolution is sufficient to separate adjacent REE. We should remark that the escape peak height corresponds only to a few KeV, but the Proportional Counter is perfectly able to handle energies above a few hundreds of eV and this poses no problem at all.

For comparison's sake a good Ge/Li Low Energy Photon Detector<sup>(10)</sup> with state-of-the-art performance would have an energy resolution in this range of about 2%, being about as adequate to resolve the REE, but would cost some ten thousand dollars, require weekly liquid nitrogen filling, be very delicate to operate and would have an effective area of only 0,3 cm<sup>2</sup>, while the proportional counter would have an area (and, hence, sensitivity for large samples) about 300 times larger. This is about the only alternative detector for REE analysis, since scintillation counters have inadequate resolution and Si/Li detectors cut-off above 20 KeV.

### III - STRUCTURE OF THE ESCAPE PEAKS

The K X-Rays consisting of multiplets  $K_{\alpha_1}$ ,  $K_{\alpha_2}$ ,  $K_{\beta_1}$ ,  $K_{\beta_2}$ ,  $K_{\beta_3}$ , etc. for both the incident and the escaping photons, the escape peaks would be very complicated indeed. Fortunately, the lines beyond  $K_{\beta_1}$  are of negligible intensity and, as can be easily verified by calculation, the lines due to  $K_{\alpha_1i} - K_{\alpha_1e}$ ,  $K_{\alpha_2i} - K_{\alpha_2e}$  and  $K_{\alpha_1i} - K_{\alpha_2e}$  are sufficiently close to each other to overlap within the resolution of the counter, resulting in a single peak, which we call  $K_{\alpha i}$ . Similarly, we call  $K_{\beta a}$  the peak resulting from  $K_{\beta_1i} - K_{\alpha_1e}$ , and  $K_{\alpha \beta}$  the one resulting from  $K_{\alpha_1i} - K_{\alpha_1e}$ . In the above, subscript  $i$  refers to the incident K X-Ray from the REE and  $e$  refers to the escaping K X-Rays of Xenon. The spectra will then consist of triplets  $K_{\alpha i}$ ,  $K_{\alpha \beta}$ , and  $K_{\beta a}$  of approximate intensities 200%, 15% and 15% respectively, resulting from the composite probabilities of detection and escape. The corresponding energies will be the difference between incident and emergent energy. The peaks corresponding to values of  $E_i$  less than  $E_0$  will of course be absent. This is the case here for all of the

La lines except  $\text{LaK}\beta_1$  -  $\text{XeK}\alpha_1$  and a small second order peak corresponding to  $\text{LaK}\beta_1$  -  $\text{XeK}\beta_1$ .  
The line  $\text{K}\alpha_{2s}$  -  $\text{K}\alpha_{2e}$  is missing for Cerium, being also energetically impossible.

#### IV -- CHOICE OF THE RADIOISOTOPE

Although  $\text{Co}^{57}$  was used in the experiments a host of other radioisotopes are adequate<sup>(11)</sup>.

They have to have an energy larger than the K-edges of the REE (that is, 63KeV), but as low as possible for maximum excitation efficiency.

Gamma emitters are normally used, but beta emitters are acceptable, although they give a higher background due to Brehmsstrahlung. Source-target combinations are also very adequate<sup>(12)</sup> and can be adjusted to discriminate against REE above desired energies, to eliminate interferences, or to simplify spectra. Other desirable properties are a long-life low-cost. A few milliCuries are more than adequate and about 10 mCi is usual. Good choices are  $\text{Co}^{57}$ ,  $\text{Am}^{241}$  (except for Yb and Lu) and  $\text{Gd}^{153}$ .

#### V -- EXTENSIONS OF THE METHOD

Since resolving power improvement derives from the proximity of incident and escaping characteristic X-Rays, many interesting combinations are possible by the choice of detector-sample combination. Scintillation Counters are poor resolution detectors to start with, and are normally unsuited for this application, although the gain in resolution would be comparable to that obtained with Proportional Counters. Solid State Detectors are probably also inconvenient since they are made of light weight elements; their escape peaks would be very low energy, and be lost in the noise.

Thus, the only attractive choice at present appears to be Proportional Counters, which can be made out of a wide variety of gases and are almost noiseless devices, both rugged and of simple operation. For instance, with a counter of Krypton we could analyse Rb, Sr, Nb and Mo, its neighbours, and calculation shows resolution improvements of 2 to 4 times, enough to resolve these elements, which is impossible conventionally with Proportional Counters. Other interesting gases would contain Pb (say, lead tetraethyl) and would allow the analysis of Bi, Th and U with an improvement in resolution ample enough to resolve them, and possibly resulting in an instrument adequate for field analysis.

#### VI -- EXPERIMENTAL

The apparatus used is shown schematically in Fig. 2. No great care was taken in optimizing the geometries of excitation or detection, and no auxiliary X-Ray filtering was used to reduce back-ground and interference. The block diagram of the electronics is shown in Fig. 3. The Proportional Counter is a standard Reuter-Stokes RSG-61, filled with 2 atm. Xenon; with Stainless Steel walls and Beryllium windows of the sealed type. The windows are not required, except for calibration of the low-energy region, since the K X-Rays of the REE are negligibly attenuated by the walls. The REE utilized were of P.A. grade and sample holders were thin-walled plastic cups. The samples were diluted in water. The source used was a 10 mCi  $\text{Co}^{57}$  made by Amersham.

## VII - DISCUSSION

Energy calibration and resolution measurement were done using the 6.4 KeV ( $\text{Fe K}_\alpha$ ) from the source and its 14.4 KeV gamma line. Resolution measured 40% at 6.4 KeV and 14% at 14.4 KeV while the manufacturer's typical values for this counter are 15.6% and 10.5%.

The poor value was later verified to be due to the broad geometry and could be improved by better collimation, but this was not done, since previous measurements were done in that geometry. Also, the count rate was so high as to spoil the resolution. Improvements could also be obtained by reducing the count-rate, using a windowless counter of better field geometry, optimizing pulse shape, using a longer and thicker tube, optimizing the high voltage, using a lower pressure tube, so as to operate at lower voltages, using a lower Z cathode material such as aluminium to give less wall fluorescence interference and a better, poorer geometry arrangement for the source and the sample. The resolution for La measured 21.5%, while prediction gives 13%. With the best construction techniques resolution improvements of up to fourfold seem possible and have been obtained by other workers<sup>(13)</sup>. The samples were of large extent and essentially infinite thickness, which amounts to about 1 cm for the REE and 10 cm for water. Note that the high penetrating power, compared to that of L X-Rays, allows the use of large samples, thus reducing sample inhomogeneity effects and relaxing positioning and sample-surfacing tolerances.

Count rates for a 1 g samples were about  $2.7 \times 10^3$  cps in the escape peak and the background (measured at the shoulders) was about  $1.4 \times 10$  cps

Sensitivity at the  $1\sigma$  level was computed<sup>(14)</sup> as about 20  $\mu\text{g}$  for a counting time of  $10^4$  seconds and is roughly constant for all REE, except La and Ce, where it is about 80  $\mu\text{g}$ . Precision computed from Poisson Statistics, was about 0.02%, and the measured value was 0.1%, probably due to positioning errors and temperature drifts, since no great care was taken in that regards.

A qualitative study of interferences was made and results compared very favorably with other techniques such as X-Ray spectrometry and Atomic Absorption. In particular, the effect

of different chemical combinations of the REE, and the addition of light elements to the sample had small effects, restricted mainly to an increase in background and reduced sensitivity, without practically any effect on the peak shapes or net peak counting rates.

Figure 4 shows the measured resolution of the counter for the 6.4 and 14.4 KeV lines of the  $\text{Co}^{57}$  source.

Figure 5 shows the background obtained from an infinite pure water sample, which is mainly due to Compton Scattering of the 122 and 137 KeV gamma-rays. The Compton backscattering peak occurs theoretically at about 80 KeV; and the observed peak at 27 KeV results from the counter cutting-off higher energy photons.

Figures 5 to 9 show the spectra of several REE Chlorides in a 10% water solution.

In Fig. 9 and 10, plotting was limited to the low energy region to save printing time, but the Compton region was essentially identical to that of Fig. 5, and gain settings were all identical, to permit fair comparison among the plots.

Figures 5 and 6 display the lack of the lines of La and Ce energetically impossible, in accord with the theoretical discussion above, but the other elements show the clearly resolved  $K_{\alpha\alpha}$ ,  $K_{\alpha\beta}$  and  $K_{\beta\alpha}$  lines predicted.

Remarkable is the similarity and simplicity of the spectra, the excellent resolution and the low background (which is the ordinate value at the extreme right) for all the 11 REE available, out of the total of 14 existing ones.

In Figure 10 a faithful superposition of spectra is made to show the excellent separation obtained for samples simulating naturally occurring combinations.

## VIII -- CONCLUSION

The method proposed is capable of analyzing naturally occurring samples of REE with excellent rapidity, sensitivity, precision, accuracy and lack of interferences and artifacts, and has distinct advantages over all other usual methods of analysis. It requires practically no sample preparation, is insensitive to chemical form and to mineralogical granulometric and geometrical effects.

In combination with spectral analysis; K-edge filtering techniques, proper choice of exciting radioisotope energy and after an optimization of counting geometry and counter resolution it is capable of large improvements. It seems also possible to extend the method by choice of an appropriate counting gas to the analytical isolation of almost every neighbouring sequence of elements, and to that of Uranium and Thorium in particular.

The equipment is simple, conventional, low-cost, rugged, consumes no gases or refrigerants, being thus adequate to industrial or field uses, especially since it is capable of remote sensing and operating through thick windows of almost any material.



### FIGURE CAPTIONS

Fig. 1 - Detection efficiency of the escape X-Rays of the REE versus the gas pressure for a 2" diameter X:non Filled Proportional Counter. Values for the other REE not shown are intermediate between the two curves.

Fig. 2 - Diagram of the Experimental Arrangement of the Apparatus.

Fig. 3 - Block diagram of the Electronics used.

Fig. 4 - Spectrum of the  $\text{Co}^{57}$  lines at 6.4 KeV and 14.4 KeV  
(a) Through the window; (b) Through the counter walls of 1 mm. thickness stainless steel.

Fig. 5 - Background for an infinite  $\text{H}_2\text{O}$  sample.  
(a) with an Al filter of 1mm thickness  
(b) without the above filter  
(c) background without sample and filter

Fig. 6 - Spectrum of a La sample - Observe the practical absence of the photopeak and the good separation of the La peaks.

Fig. 7 - Spectrum of a Ce sample with the peaks identified  
(a) Expanded  
(b) Normal Scale

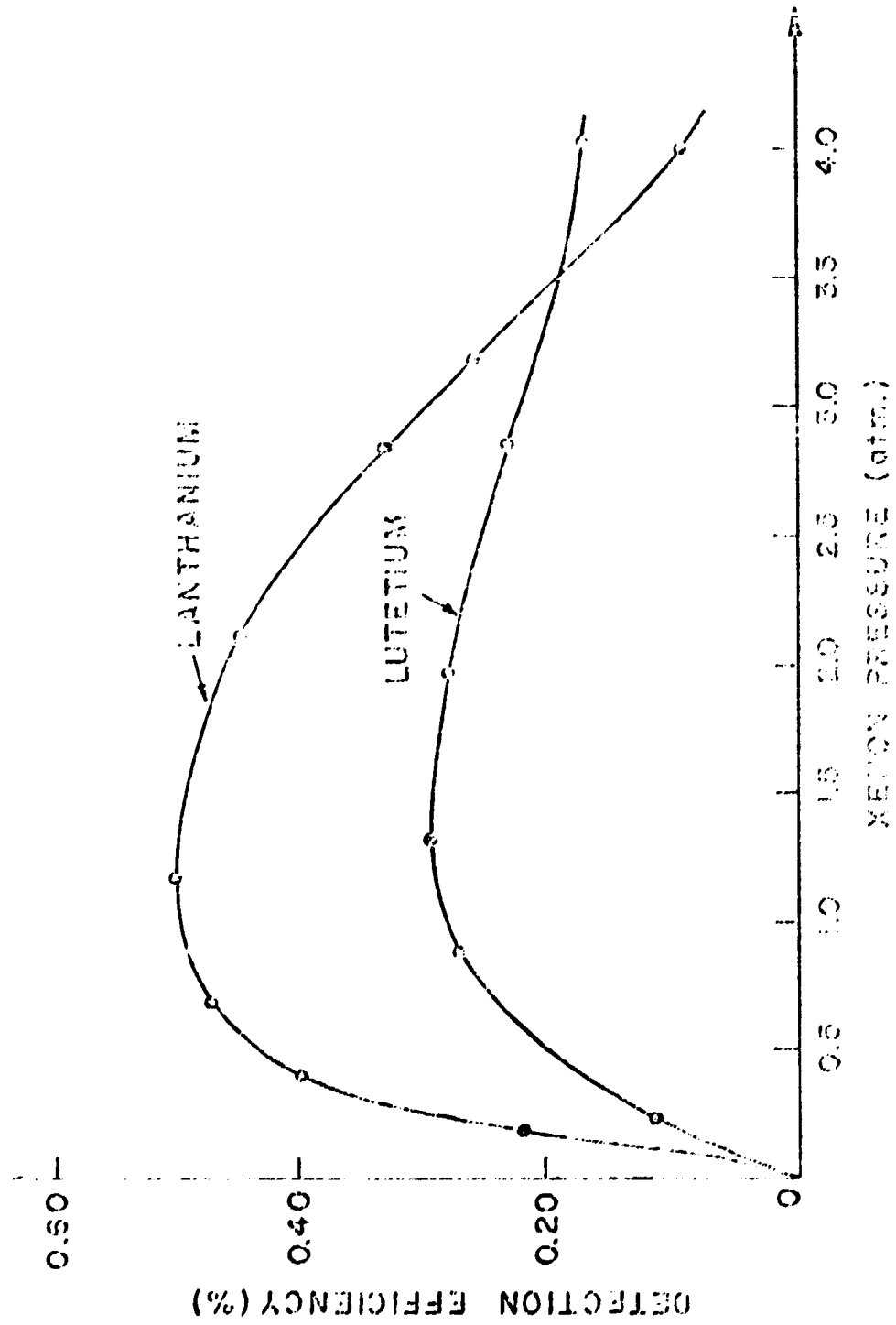
Fig. 8 - Comparison of Ce and La spectra.

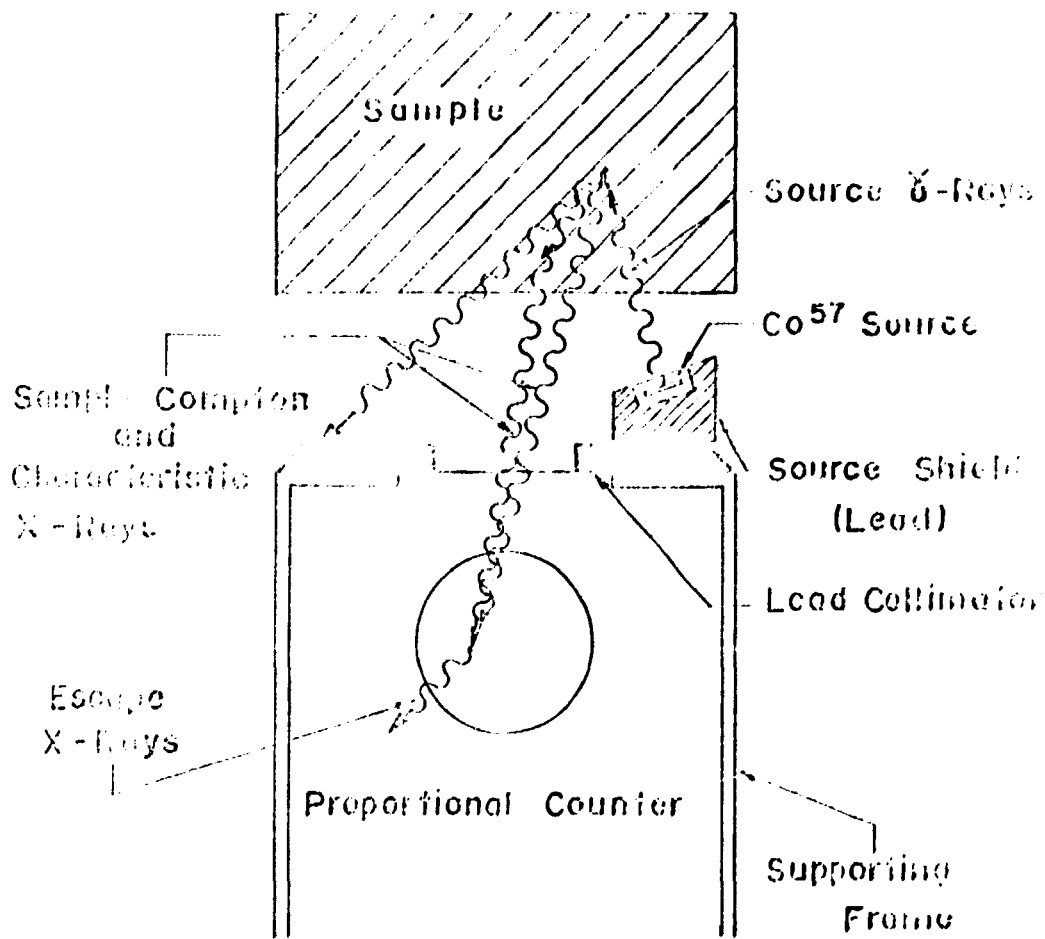
Fig. 9 - Spectra of the 11 REE available. All scales and counting times are identical and the spectra have been displaced to avoid superposition. The peak structure and energy coincides precisely with the calculated values. Observe the good separation amongst the lines.

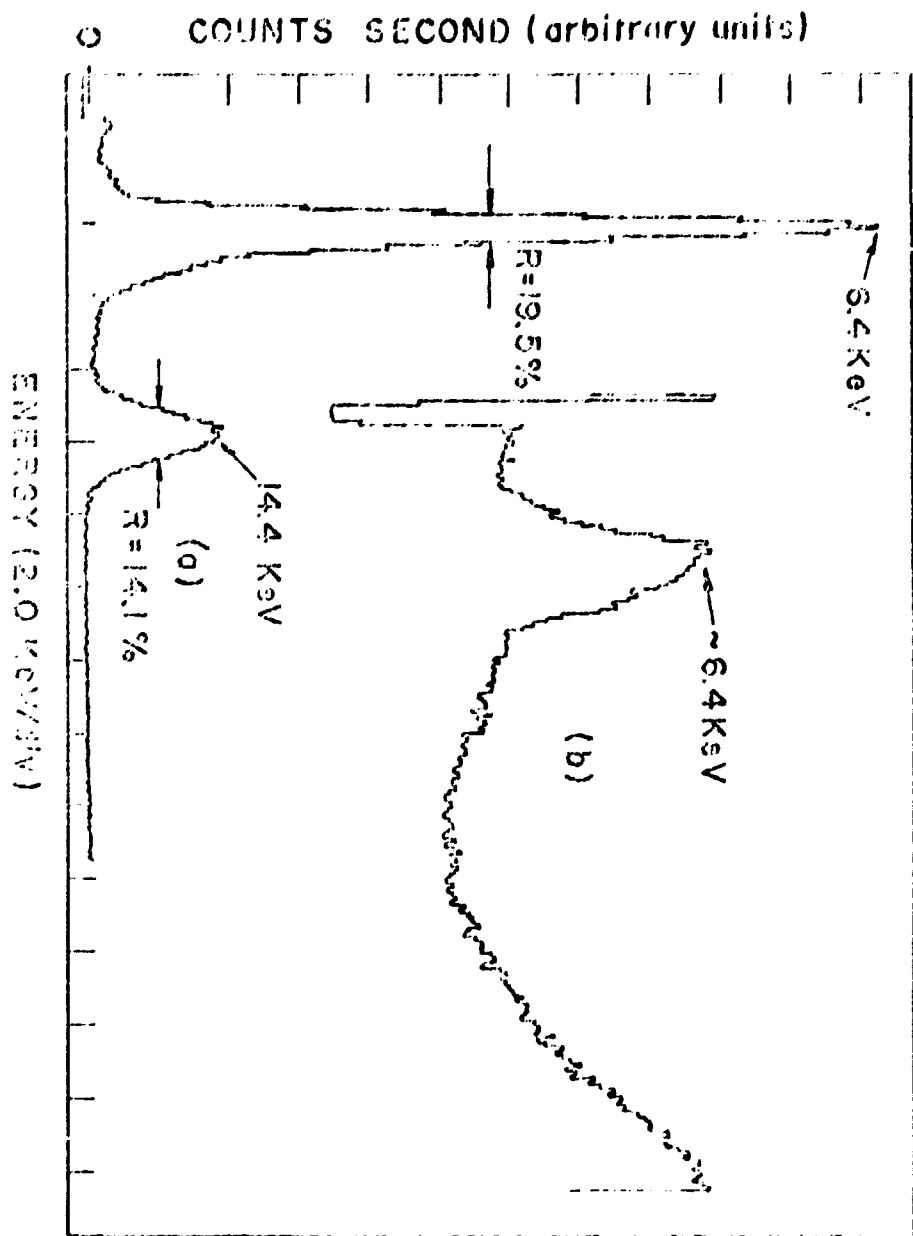
Fig. 10 - Superposition of some spectra of Fig. 9, simulating the main composition of (a) Apatite or Monazite (b) Xenotime (c) Equimolar mixture of Nd and Sm (d) Equimolar mixture of Dy and Er. Observe that resolution is amply sufficient to separate the peaks of these simulated natural compositions of light and heavy REE minerals.

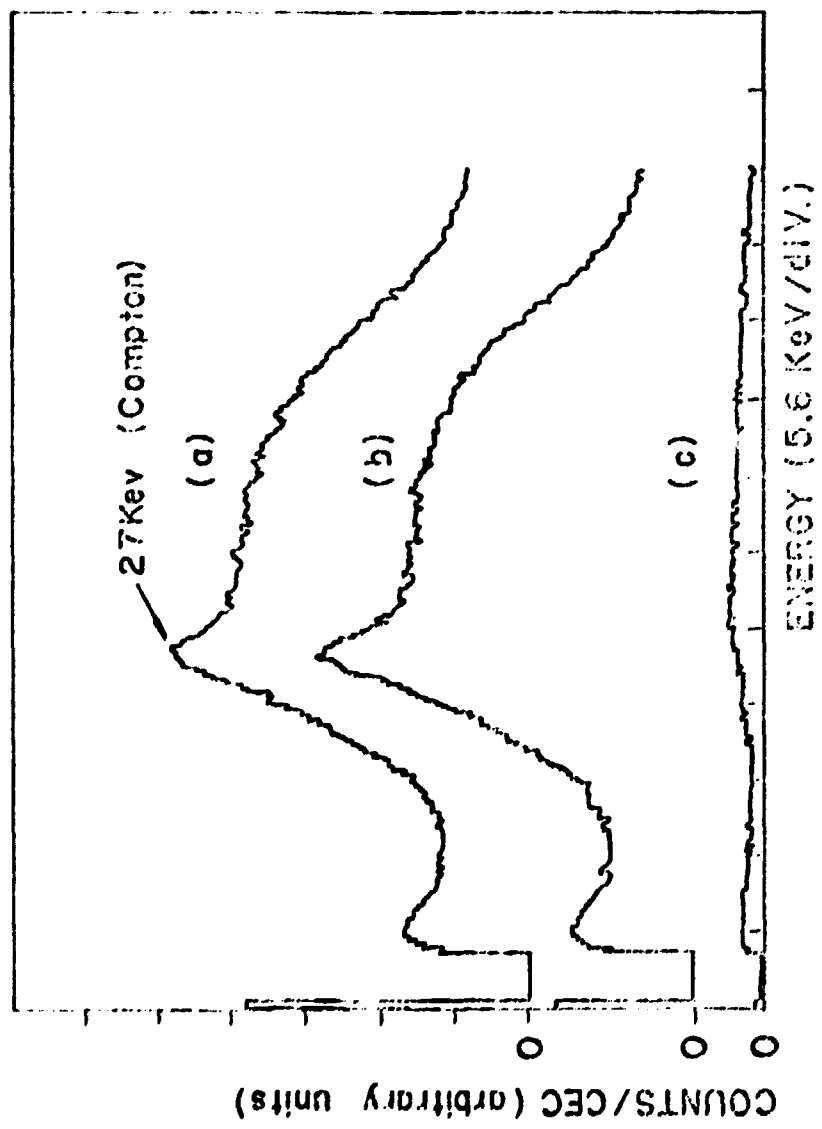
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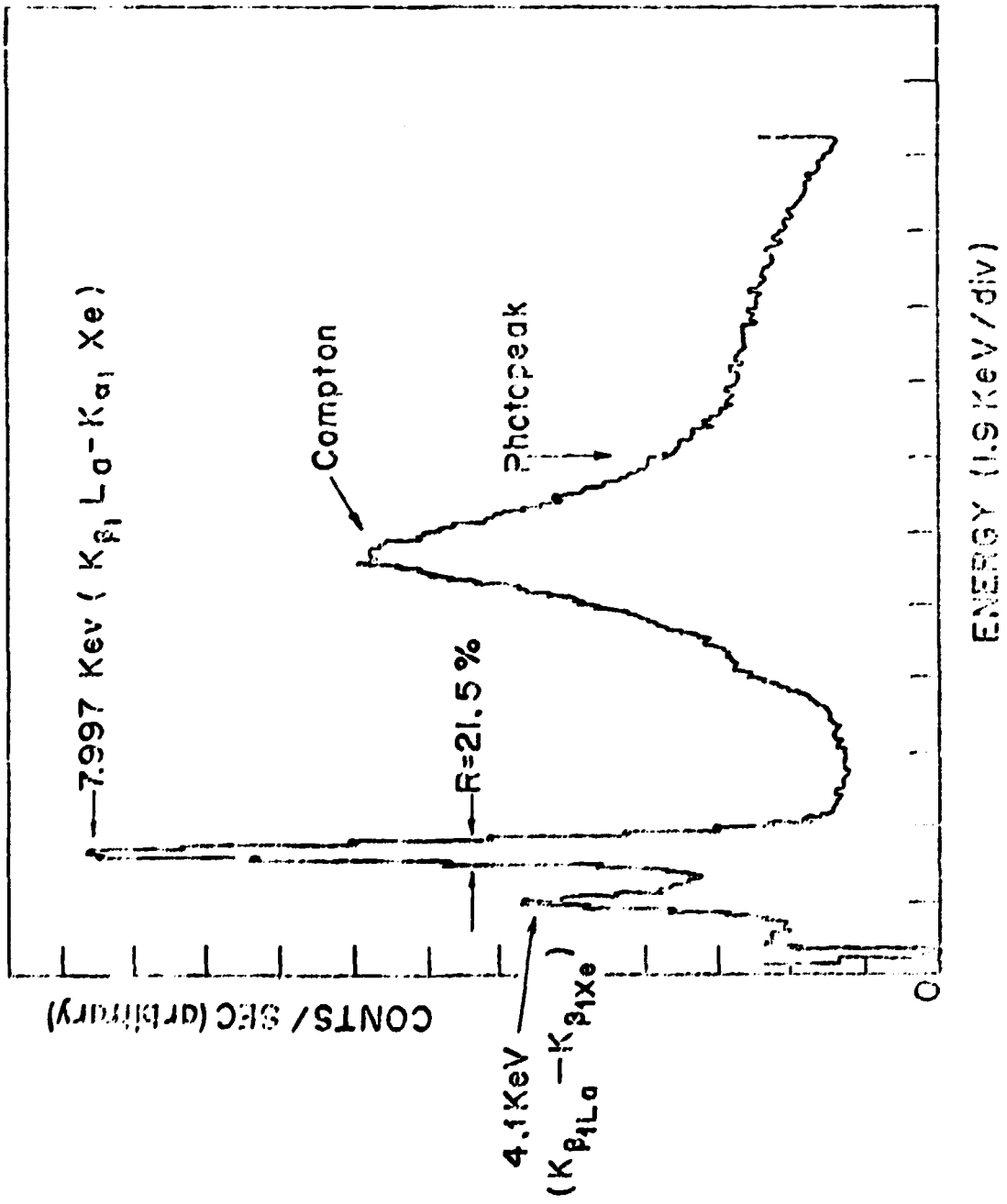
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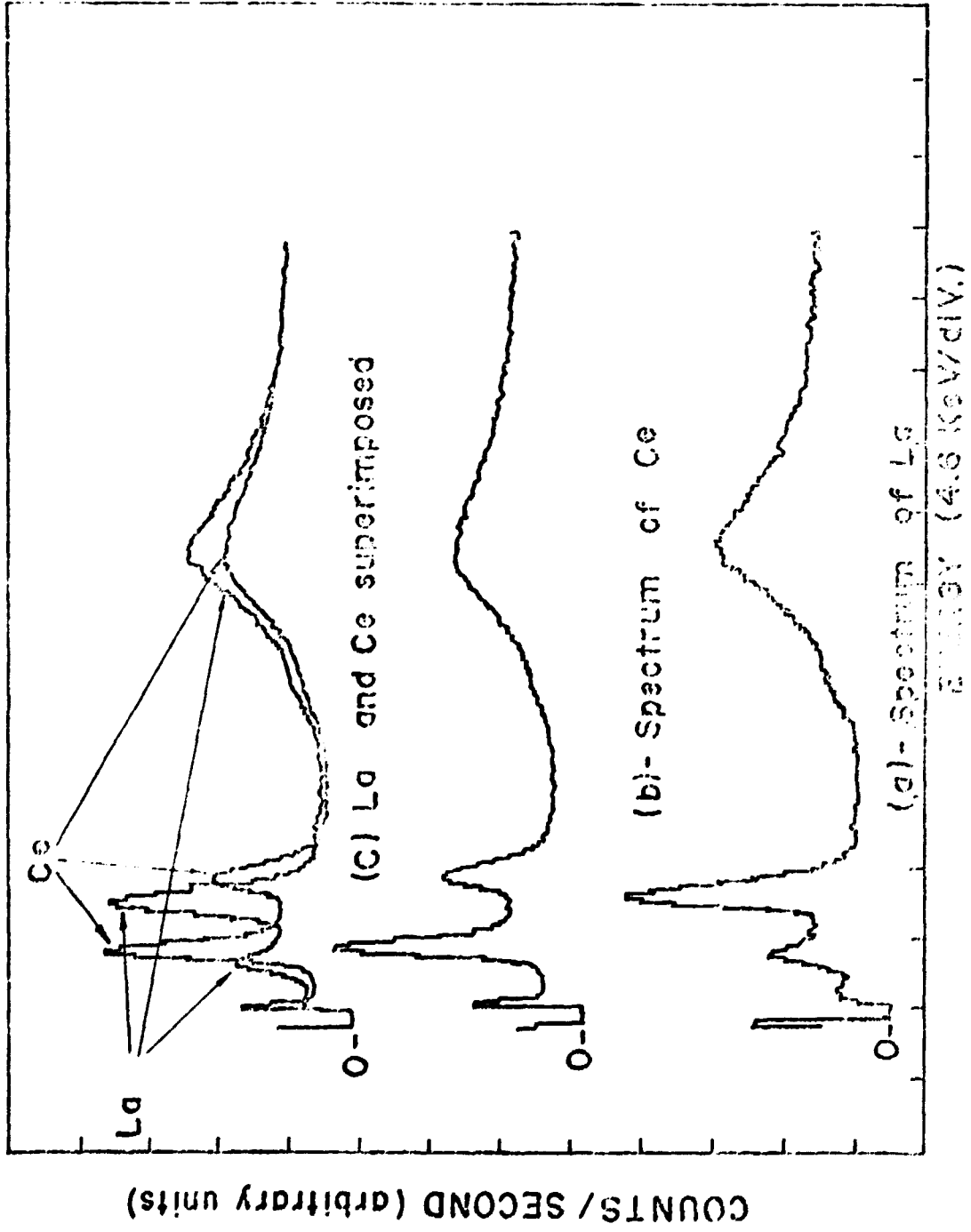




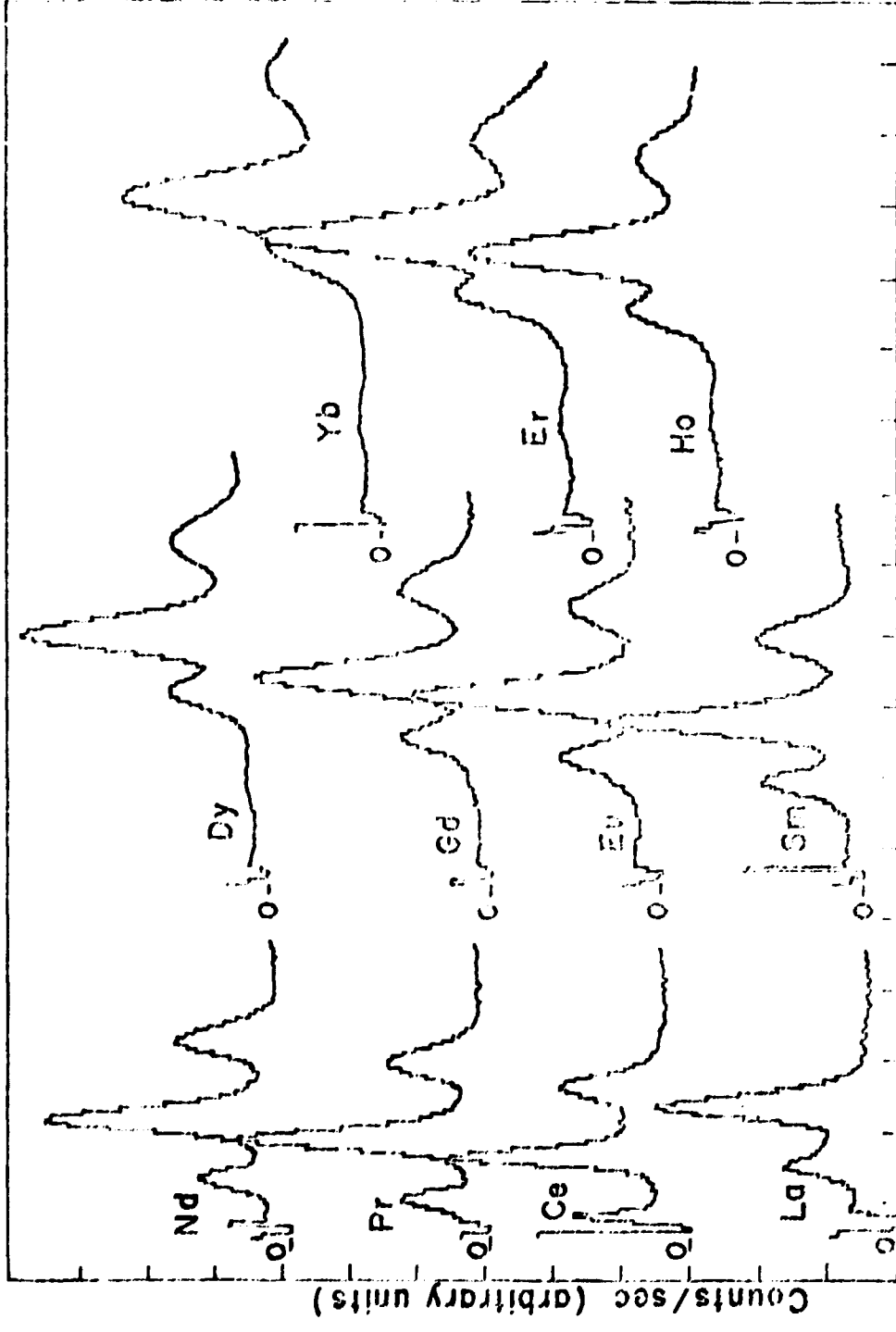












ENERGY (4.0 KeV / DIV)

