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ANALYSIS OF RADIOACTIVE WASTE SAMPLES BY ION CHROMATOGRAPHY-ICP/MS

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ABSTRACT: A comprehensive ion chromatography (IC) with beta-counting (beta) and inductively coupled plasma mass spectrometry (ICP/MS) detection approach has been developed to separate and detect 20 radionuclides in a Hanford waste tank sample. The IC separation was performed using a multi-functional group (anion/cation) resin and eluents of oxalic acid, diglycolic acid, and hydrochloric acid. Shorter-lived radionuclides were detected by a solid-state beta scintillation counter on-line with the IC separation. Mass spectrometry detection using an efficient and robust plasma ionization source provides isotopic discernability for both stable isotopes and long-lived radioactive species. Effective separation of over 47 elements and 160 isotopes was obtained from a single-elution scheme lasting 70 min. Automated IC separations provide the potential for rapid isotopic and radionuclide analysis of complex radioactive waste, using minimal sample and reagent volumes and reducing personnel exposures.

KEY WORDS: ion chromatography, ICP/MS, IC-ICP/MS, radionuclides, solid-state beta scintillation, contained ICP/MS, online separation, radioactive waste

Introduction

Since its inception, inductively coupled plasma mass spectrometry (ICP/MS) has intrigued the radioanalytical chemist with its promise for the concurrent analysis of both stable and radioactive isotopes. With routine detection limits in the sub-pg/mL (ppt) range, ICP/MS has been effectively used from the outset to measure stable isotopes and long-lived radionuclides of uranium and thorium [1]. Limits placed on the allowable level of radioactivity in samples to be analyzed by ICP/MS have generally restricted radioactive analysis to these primordial radionuclides and their progeny. As detection limits improved, many investigators focussed on measuring additional radionuclides by ICP/MS [2,3,4,5], leading to a variety of designs for containment systems and instrument modifications [6]. These instruments have been routinely used to measure both radionuclides and stable elements in many sample types, including contaminated waters and soils, nuclear fuel, and solutions containing radiolabeled compounds. Molecular, isobaric, and matrix-element interferences have limited the direct application of this technique for unequivocal radionuclide characterization. However, these interferences can be resolved by interfacing an elemental separation technique such as ion chromatography (IC) with a suitably contained ICP/MS.

No longer restricted to "nonradioactive" samples, a radiologically contained instrument is capable of measuring virtually any radionuclide; however, the inverse relationship between activity and half-life dictate that activity measurements are more sensitive for shorter-lived radionuclides while atomic detection by ICP/MS is superior for longer-lived radionuclides [2]. Radioactive samples often contain a complex mixture of anthropogenically-produced radionuclides with matrix components consisting of numerous elements with natural isotopic compositions. Isotopic abundances of elements (particularly fission produced) cannot be ascertained *a priori* in such mixtures. Consequently, IC separation with subsequent detection by ICP/MS and beta counting has been applied to clearly determine isotopic compositions of these complex radioactive wastes. Elemental, long- and short-lived radionuclides and isotopic abundance from a single sample are determined and presented in this work.

Experimental

Objective

The purpose of this experiment was to demonstrate the breadth and versatility of elemental and isotopic separation possible in a multi-dimensional, IC-beta-ICP/MS analysis scheme. A radioactive waste sample from Hanford Tank SY-101 was used to illustrate this technique.

Procedure

Separations were achieved with a commercially-available ion chromatograph. All analyses were conducted on an ICP/MS and a solid-state scintillation beta counter. The entire system was modified with suitable containment measures for radioactive sample introduction. The schematic of the IC configuration used in this work is shown in Fig 1. The beta detector was equipped with one 600-microliter solid-state scintillation cell and two electronic detector channels having separate discriminator adjustments. The separate channels make it possible to differentiate the energies of some radionuclides (i.e., ^{154}Eu and ^{155}Eu).

Automated elemental separation was produced by the gradient eluent program as depicted in Fig 2. Initially, an isocratic eluent of 25 mM oxalic acid was pumped through the separator column at a rate of 2 mL/min to convert the column to the oxalate form. A sample solution having a free 0.05 M HCl concentration, which provides for the formation of both anion and cation chloro-complexes [7], was loaded by an autosampler into a sample loop located on the sample injection valve. The sample loop was then switched on-line with the separator column. The complex ions were then separated and eluted from the column into the ICP/MS and/or a beta detector using the illustrated gradient program.

Due to limitations in the available software for chromatographic (i.e., time-based) analysis, data were acquired in files containing a maximum of 99 samples (time slices) per file name (the 99 samples per file is a software platform limitation.) Each time slice consisted of 15 sec of mass spectrometric data acquisition (mass range 37-247 amu) followed by 9 sec of data transfer and processing for a total of 0.4 min. These data were graphed in three dimensions, i.e., element (time), isotope (m/z), and intensity (counts per second), as illustrated in Fig. 3, for the case of light rare-earth elements (REE).

Results and Discussion

Elution conditions for this separation used an aqueous multi-element standard solution, having an elemental concentration of 100 ng/mL and buffered with hydrochloric acid having a 0.05 M free-acid concentration. Elution times and peak widths determined using ICP/MS are tabulated in Table 1 and illustrated graphically in Fig 4. The chromatographs illustrate the quality of the separation and detection. The Hanford SY-101 tank core sample was prepared using a sodium-peroxide fusion that was dissolved, diluted, and then buffered with hydrochloric acid to 0.05 M free acid. This sample was loaded and separated in the same manner as the standard solution. Table 1 illustrates the elution characteristics and detection of 36 natural elements by IC-ICP/MS, and the determination of 20 radionuclides (11 by beta detection and 14 by ICP/MS) for this sample. Because analyte response may change with the changing IC eluent stream, it is crucial that many data "time slices" be scanned and transferred to the acquisition computer as expediently as possible. Data-acquisition constraints limited resolution and ultimate sensitivity. Improvements in acquisition software for transient signals will allow the recording of individual sweeps for optimal peak definition (peak height and peak area) and improved peak resolution. Comparing the elemental elution times of the standard element solution with the Hanford tank sample gives an indication of matrix effects. In some cases, both elution time and order have been altered. When nonselective detectors (i.e., conductivity, variable wavelength, etc.) are used to detect eluting peaks, precise retention times are required and are usually assumed or determined via co-chromatography with spiked standards. Matrix constituents such as acids, bases, organic, salts, etc., and the free-acid concentration of the sample solution have significant effects on the analyte-retention properties. By using a selective detector (i.e., ICP/MS), sample matrix effects on peak retention times do not obstruct the identification of eluting peaks.

The beta-emitting radionculides observed using the beta-scintillation detector are illustrated in Fig 5. The elemental elution times obtained from the Hanford tank sample by ICP/MS were used to identify the specific radionuclides. The incorporation of the beta-scintillation device is used to complement ICP/MS determination of long-lived isotopic abundance by detection of long- and short-lived radionuclides. Short-lived radionuclides measured with the beta detector but undetected with ICP/MS include parent ^{144}Ce ($t_{1/2}$=285 day) and daughter ^{144}Pr ($t_{1/2}$=17 min) as illustrated in Fig 6. These radionuclides existed in secular equilibrium at the time of sample injection. Because ^{144}Pr was continually being produced by the ^{144}Ce, complete separation of Ce from Pr could not be achieved, thus causing an apparent broadening of the ^{144}Ce peak. The difference in beta energies and resulting difference in detector efficiencies were responsible for the smaller peak height of Ce.

Despite the demonstrated effectiveness of sequential elemental separations, IC-beta-ICP/MS requires further development to achieve accurate and reproducible quantitation, reduce sample matrix effects, and obtain real-time data acquisition. In conventional ICP/MS analysis, an internal standard is usually added to correct for instrument drift and sample-matrix effects. These effects are even more significant in IC-ICP/MS because the eluent composition (and therefore the instrument response) is typically changing. The effects of changing eluent on several REE signals were evaluated by analyzing the static response of a rare-earth standard in different eluent compositions of oxalic acid and diglycolic acid solutions. Fig. 7 illustrates the intensity changes with different eluent concentrations. These changes can be caused by several factors, including droplet size formation and transport, nebulization efficiency, and plasma ionization conditions. Internal standard corrections are therefore required for this technique. An internal standard could be added after the IC separation (post column addition), and in a manner that does not induce significant dilution or peak broadening. We believe that the spray chamber produces a comparatively high degree of peak broadening and that introduction of an internal standard at the point of nebulization would not provide any further broadening of the measured signal. Attempts to effect such an internal standardization scheme for improved analytical results will be reported in future work.

Perhaps the greatest advantage of the IC-ICP/MS interface is its ability to unequivocally determine isotopic abundances by removing virtually all potential polyatomic and isobaric interferences. In Fig. 8, isotopic data, taken from seven consecutive time slices spanning ~3 min total and corresponding to the separation of Sm in a Hanford SY-101 tank sample, were plotted as a partial mass spectrum; the peak resolution observed is due to the elemental resolution of the IC rather than the mass resolution of the quadrupole. Compared to that of natural Sm (overlaid as black bars for comparison purposes), the isotopic abundance of the Sm present in the tank sample was far different, due to the nuclides' derivation from nuclear processes (e.g., fission, activation, decay, etc.). Although it demonstrates the technique's efficacy in isolating an element for definite isotopic abundance determination, Fig. 8 also illustrates the rather poor points-per-peak fidelity obtained using the current method of data acquisition. It is anticipated that improvements in time-resolved analysis software will eventually provide at least 2 to 3 times more data points during the same time period.

Conclusions

A contained IC-ICP/MS and/or IC-ICP/MS-beta technique for determining the elemental and isotopic composition of radioactive samples is demonstrated. The use of a selective detector (i.e., ICP/MS) is crucial for elemental identification in light of significant sample and preparation matrix effects on the elution patterns of complexed ions. Currently available time-based inorganic acquisition software is inadequate for the ion-chromatographic conditions of this type of separation, i.e., long elution times, large number of files, and long data-transfer times (9 sec) with respect to eluted peak-height and peak-widths. This work demonstrates some of the great potential and some of the problems of IC-beta-ICP/MS on an elemental and isotopic analysis technique for complex radioactive samples. Additional work in this area is continuing.

Acknowledgments

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TABLE 1. Element elution times for aqueous standard and SY-101 sample

Aqueous Standard IC Calibration			SY-101 Hanford Tank Sample				
Element	Elution Time	Peak	Element	Elution Time	Radonuclide		Interferences
	Minutes	Width		Minutes	ICP/MS	Beta	
Sb	1.1	1.4	Te	0.5			Sn, Sb, Xe
Rh	1.4	1.7	Fe	1			Cr, Ni, ArO, ArN
Se	1.4	0.7	Np	1	^{237}Np		
Ru	1.4	1	Ru	1			Zr, Mo, Pd,
Fe	1.4	1	Rh	1			
Cr	1.8	1.4	Sb	1.1			Te
Te	1.8	1.1	Cu	1.4			
Pb	2.1	2.9	Pb	1.4			Hg
Rb	2.5	1	Cs	1.9	^{134}Cs, ^{135}Cs, ^{137}Cs		Ba, Xe
Cs	2.5	0.7	Rb	1.9			Sr
Cu	2.8	0.4	Cd	2.8			Pd, In, Sn, ZrO, MoO, NbO
W	3.2	2.5	Mn	2.8			
Mo	3.2	4.4	Co	3.8		^{60}Co	Ni
Cd	3.9	1	Sn	5.3			In, Cd, Te
Mn	3.9	1	Pu	5.3	^{239}Pu	^{241}Pu	
Co	7.1	1.8	Zn	6.2			Ni, Ge
Sn	7.9	6.8	La	6.7			Ba, Ce
La	9.7	2.1	Ni	7.7			Cu, Fe, Zn
Zn	11.1	1.5	Ce	8.1		^{144}Ce	Ba, La, Nd
Re	12.2	3.2	Pr	10.2		^{144}Pr	
Ce	13.2	2.8	Nd	13.6			Ce, Sm, BaO
Ni	15	1.4	Tc	18.1	^{99}Tc		Ru
Pr	17.5	2.9	Pm	18.6	^{147}Pm	^{147}Pm	Sm
Nd	21.1	1.8	Am	19.7	^{241}Am		
Pm	23.2	1.8	Sm	20.8	^{151}Sm	^{151}Sm	Nd, Gd, Eu, BaO
Am	25	1.8	Eu	21.9		^{154}Eu, ^{155}Eu	Gd, BaO, BaOH
Sm	27.2	1.8	Gd	22.5			
Eu	29	1.4	Y	24.7		^{90}Y	Zr, Sr,
Gd	30	1.5	U	48.5	^{235}U, ^{236}U, ^{238}U		
Tb	33.9	1.8	Hf	48.5			Yb, Lu, Ta, W, ReeO,ReeOH
Dy	36.4	1.8	Nb	48.5			Zr
Y	37.4	1.5	Ta	48.5			Hf, W, ReeO,ReeOH
Ho	38.5	2.1	Zr	48.5			Nb, Mo, Ru
Er	41.4	1.8	Sr	49.5	^{90}Sr	^{90}Sr	Kr, Rb, Zr
Tm	45	2.1	Ba	52.9			Te, Xe, Te, Cs, La, Ce
Yb	46.4	2.9	Th	70.1	^{232}Th		
Lu	46.8	2.9	Cr	ND			Ti, V, Fe, Plasma
Ta	49.7	4.7	Se	ND			Br, Plasma
Zr	50	4.4	Pd	ND			Ru, Cd, Ag, ZrO, NbO, MoO,
Nb	50	4.4	Pt	ND			Os, Hg
Hf	50	4.4	Tb	ND			ReeO, ReeOH
U	52.2	2.2	Dy	ND			Gd, Er, ReeO, ReeOH
Sr	52.6	1.9	W	ND			Hf, Ta, Os, ReeO, ReeOH
Ba	57.7	9	Re	ND			ReeO, ReeOH
Pd	59.5	1.8	Mo	ND			Zr, Ru, Nb
Pt	59.8	2.9	Yb	ND			Er, Lu, Hf, ReeO, ReeOH
Th	71.6	9.3	Lu	ND			Yb,Hf, ReeO, ReeOH
			Tm	ND			ReeO, ReeOH
			Ho	ND			ReeO, ReeOH
			Er	ND			Dy, Yb, ReeO, ReeOH

Figure Captions

FIG. 1 -- IC-beta-ICP/MS system configuration. A switchable valve directs column effluent to either ICP/MS or beta detectors.

FIG. 2 -- The gradient elution program used for this separation consists of three steps. First, an isocratic oxalic acid eluent for weakly held complex ions; second, an oxalic acid/diglycolic acid gradient for rare-earth and actinide separation; and finally, a hydrochloric acid gradient for strongly-held complex ions.

FIG. 3 -- Separation of light rare-earth elements in SY-101 Hanford tank sample showing 3-dimensional information. Note inter-element separation and isotopic detail for Ce and Nd analytes.

FIG. 4 -- Elution profiles of 36 elements, using a single sample injection of an aqueous multi-element standard. Data for this separation are separated in groups for illustrative purposes.

FIG. 5 -- Detection of long- and short-lived radionuclides in a Hanford SY-101 tank sample using a beta detector on-line with IC. In-column production of the daughter ^{90}Y from the parent ^{90}Sr is observed until the elution of Sr.

FIG. 6 -- The detection of short-lived radionuclides not detected by ICP/MS (^{144}Ce and ^{144}Pr) using IC-beta separation and detection. Different beta energies and detection efficiencies account for different relative responses.

FIG. 7 -- The response of rare-earth elements are shown to be suppressed using a gradient elution of oxalic acid and diglycolic acid. The addition of a post-column internal standard should be used for quantitative analysis.

FIG. 8 -- The separation and detection of samarium isotopes in a Hanford SY-101 tank sample using IC-ICP/MS. This separation provides clear observation and determination of Sm isotopic

abundance by removing all isobaric (Nd, Pm, Eu and Gd) and polyatomic interferences (BaO, LaO, CeO).

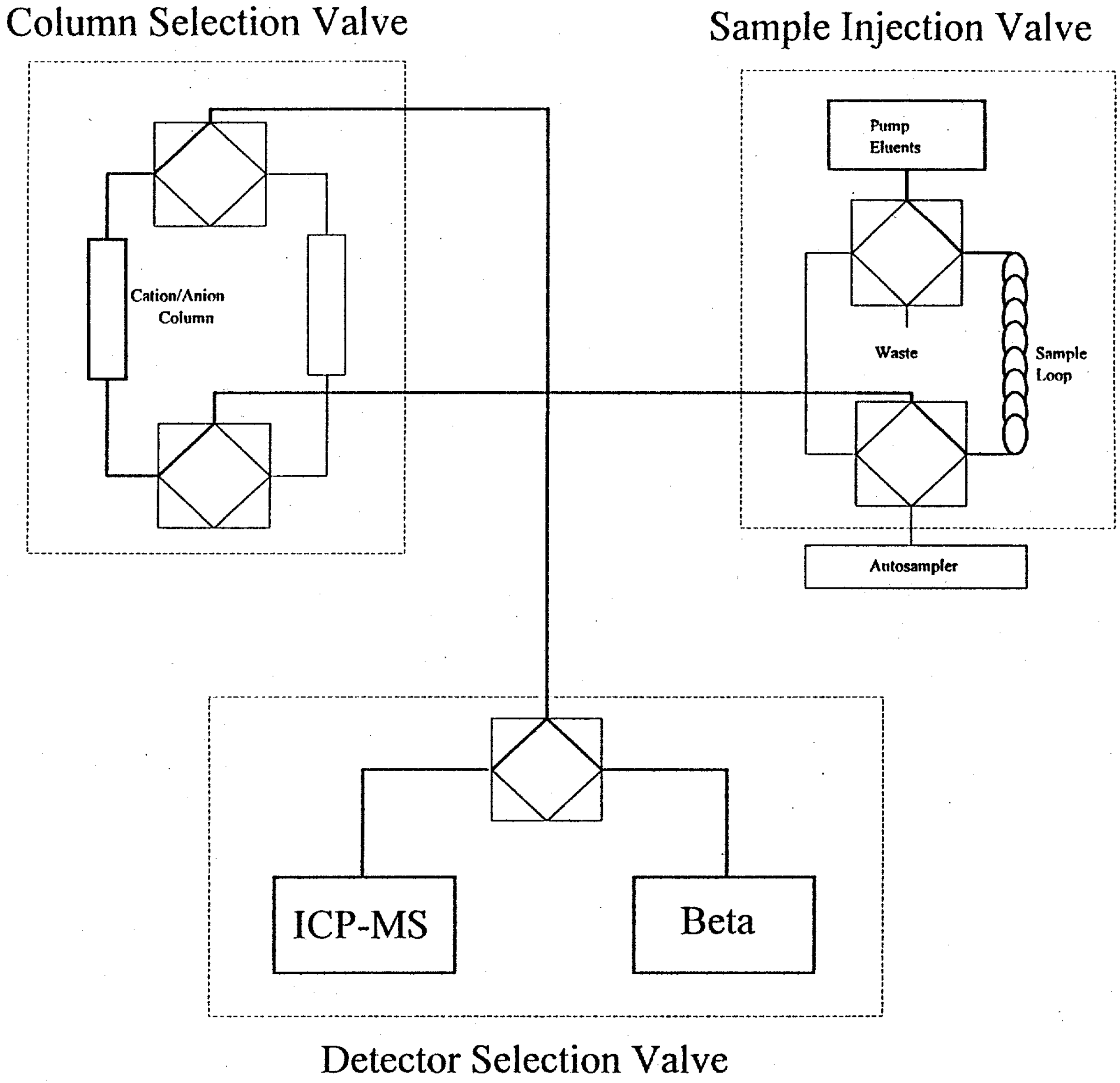

Fig. 1 - Farmer et. al.

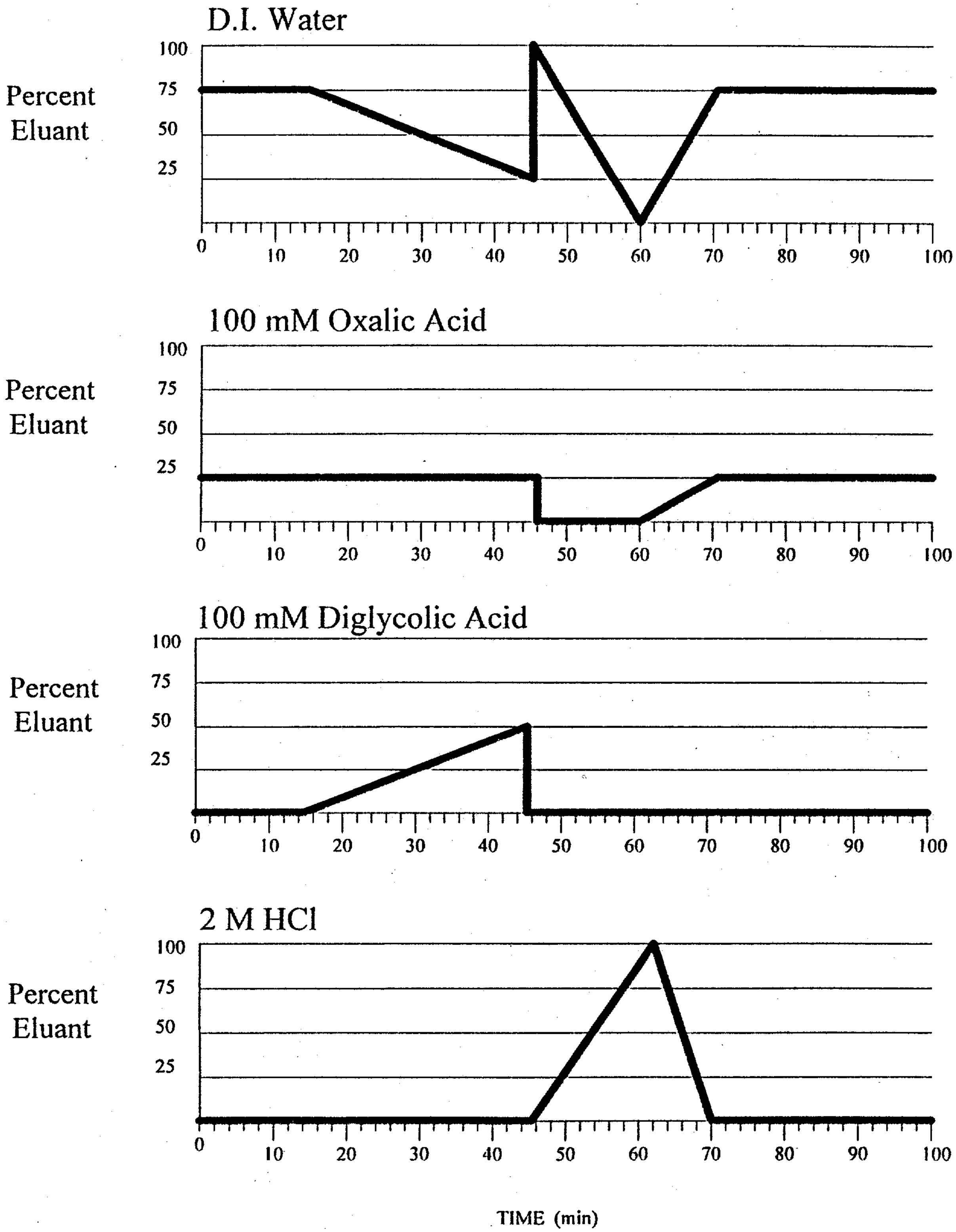

Fig. 2 - Farmer et. al.

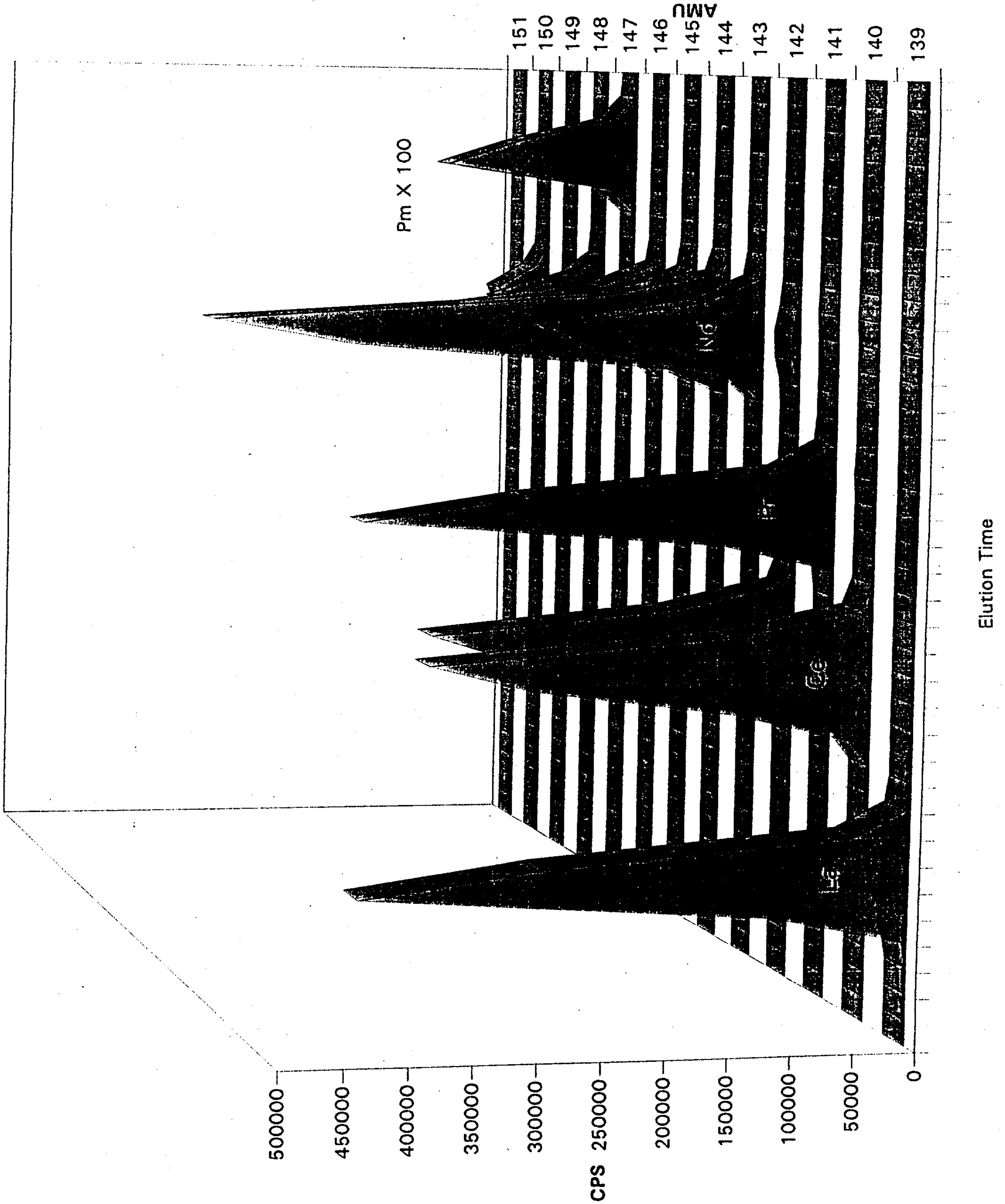

Fig. 3 - Farmer et. al.

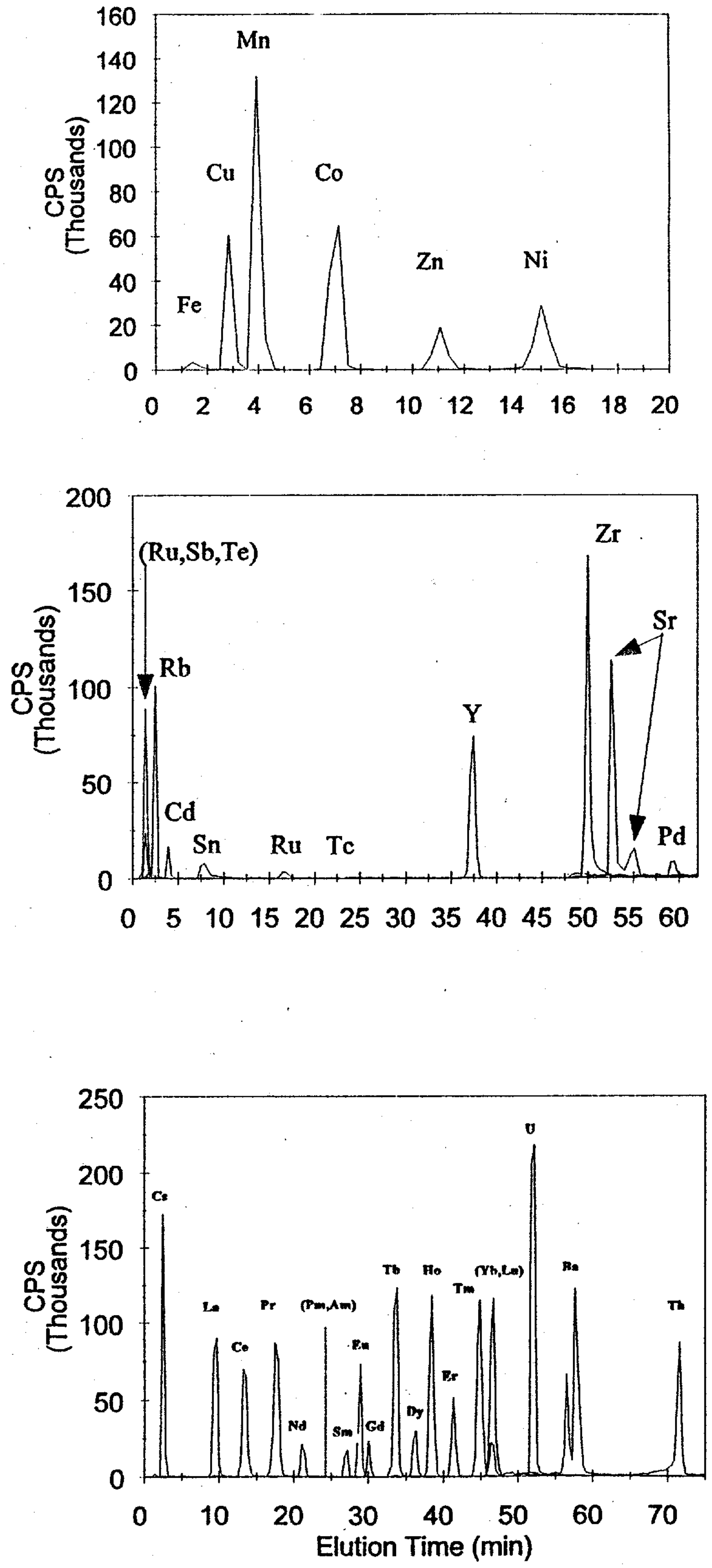

Fig. 4 – Farmer et. al.

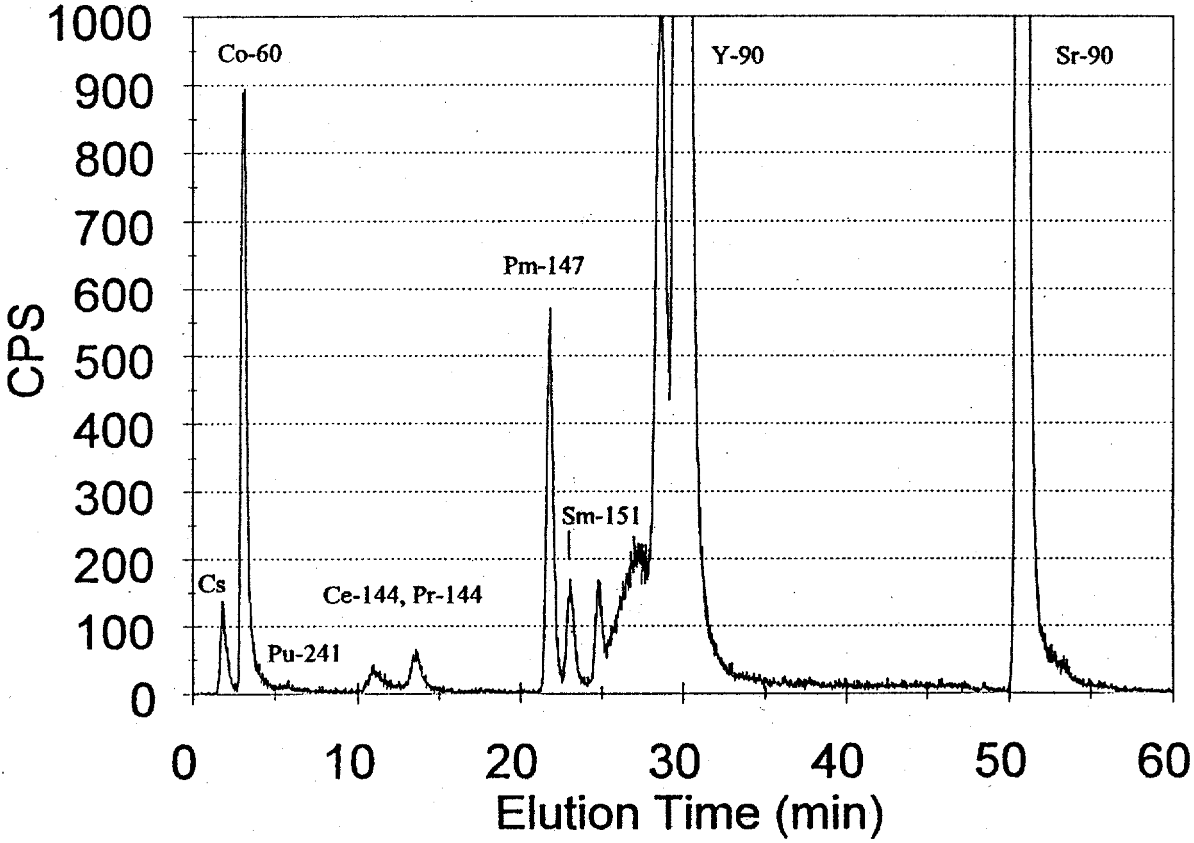

Fig. 5 - Farmer et. al.

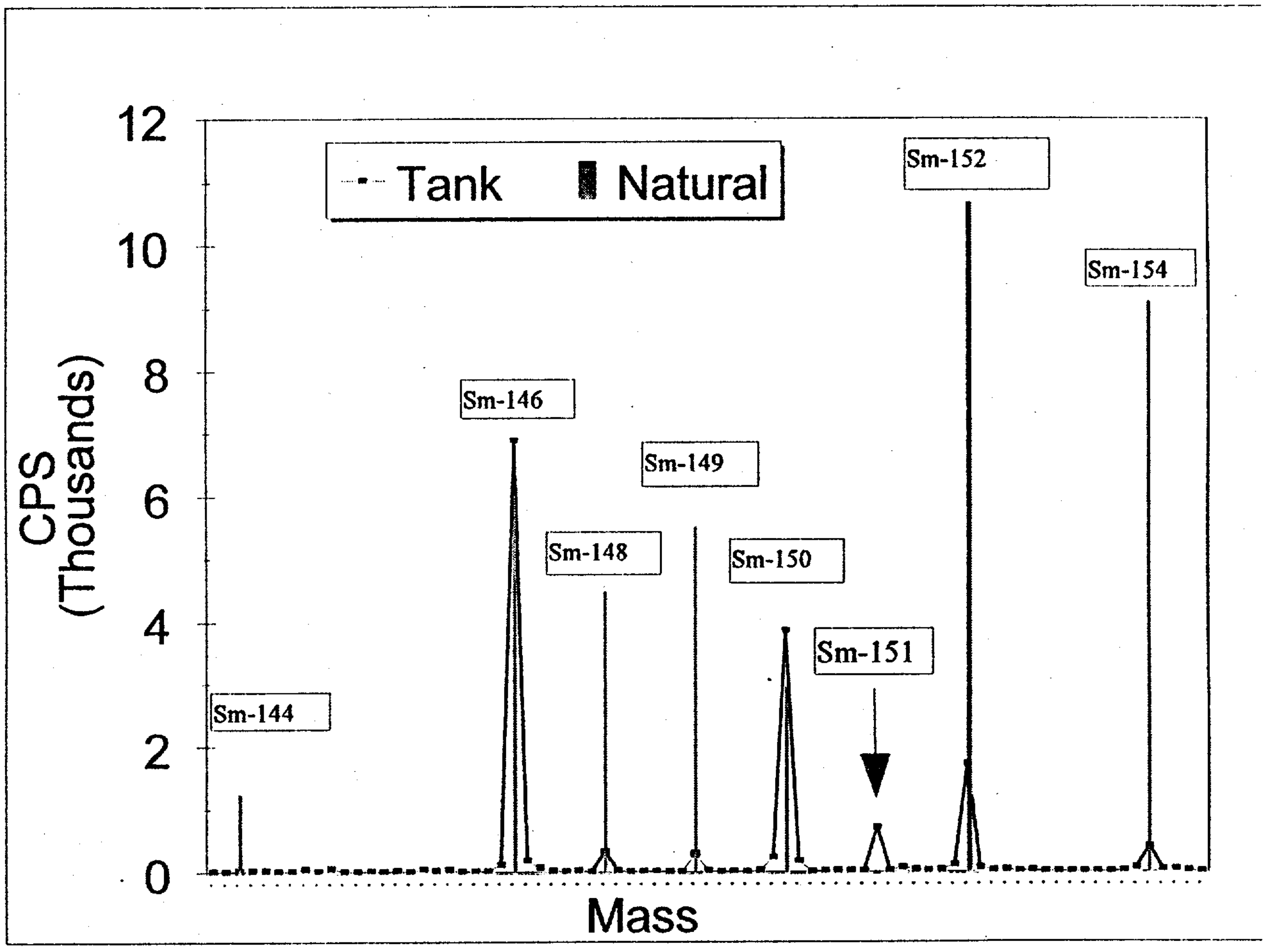

Fig. 6 - Farmer et. al.

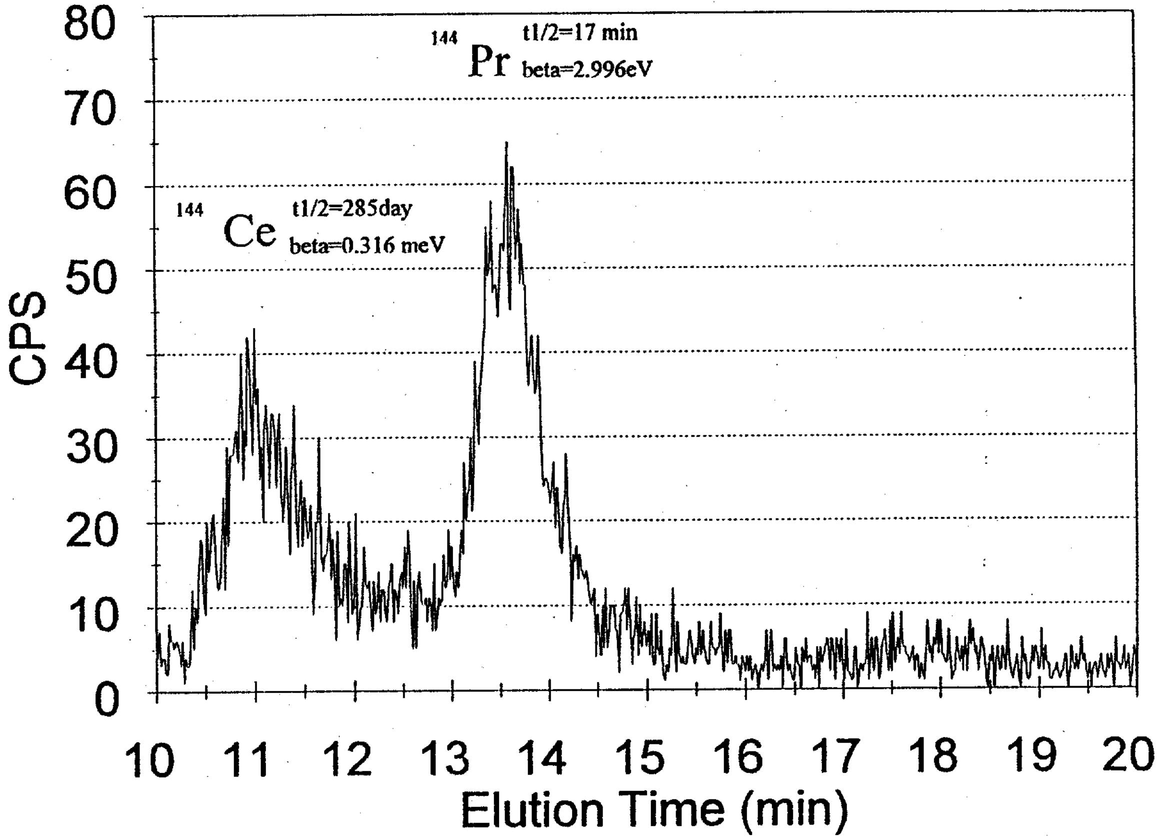

Fig. 7 – Farmer et. al.

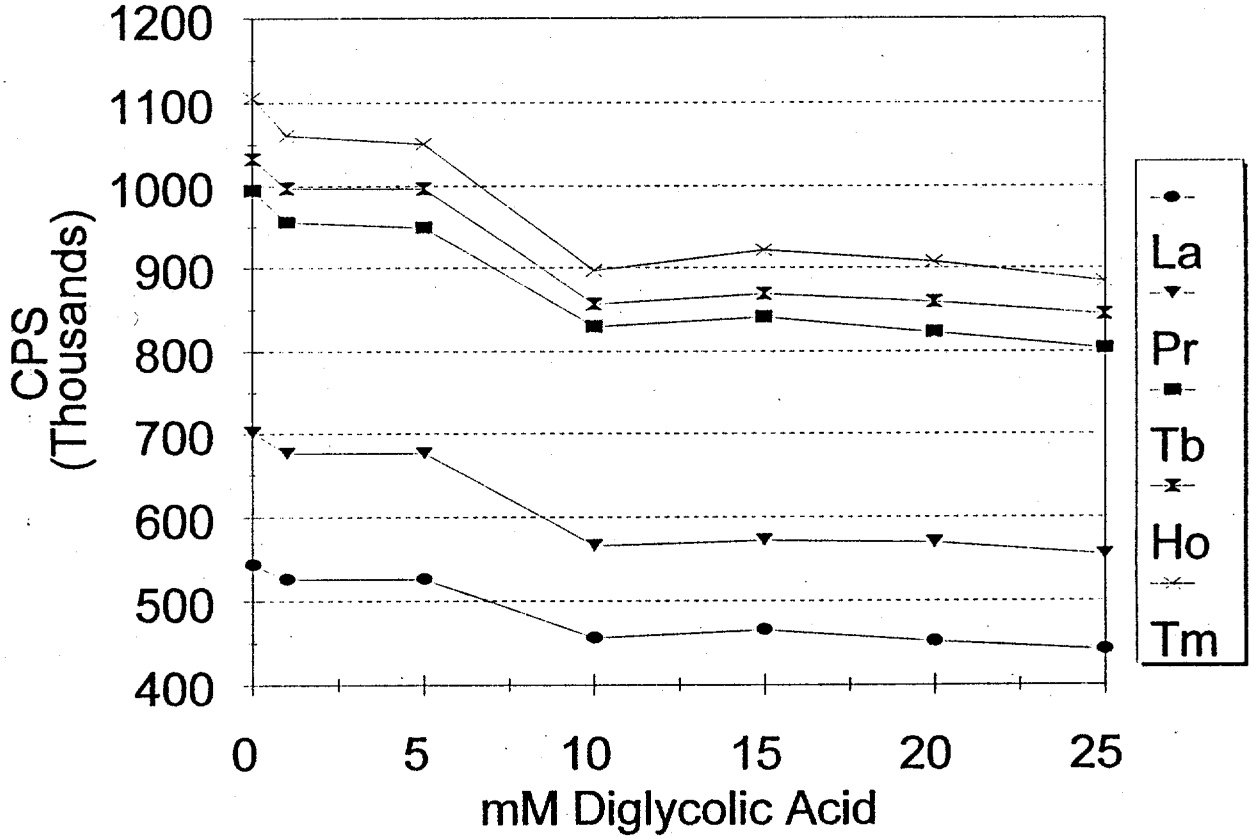

Fig. 8 - Farmer et. al.