# Vaporization of Radium and Other Alkaline Earth Elements in Electrothermal Vaporization Inductively Coupled Plasma Mass Spectrometry

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Reported are the mechanism of vaporization and optimum experimental conditions for the determination of Ra and other alkaline earth elements (Be, Mg, Ca, Sr and Ba) by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). Calculated and published data along with new experimental results suggest that these elements are vaporized from the surface of the graphite tube as oxides. These oxides are then transported to the argon plasma where dissociation and ionization take place. Appearance temperatures and maximum pyrolysis temperatures obtained experimentally generally agree with values obtained using graphite furnace atomic absorption spectrometry (GFAAS). For Ra, the optimum pyrolysis and vaporization temperatures were 1400 and 2500 °C, respectively. Diluted (1:500) seawater, used as a physical carrier, was effective in improving sensitivity when used in small quantities, but caused significant suppression of the Ra signal when the analyte was co-vaporized with quantities of salt in excess of 40 µg. An absolute limit of detection of 1.7 fg was obtained corresponding to 34 fg ml$^{-1}$ in a 50 µl sample.

**Keywords:** *Alkaline earth elements; electrothermal vaporization; inductively coupled plasma mass spectrometry; radium*

Of the four naturally occurring isotopes of Ra, $^{226}$Ra is the most abundant having a half-life of approximately 1600 years. The other isotopes are of lesser importance since they are not as persistent with half-lives of 6.7 years for $^{228}$Ra, 11.7 days for $^{223}$Ra and 3.64 days for $^{224}$Ra. No stable isotope of Ra exists. Radium found in nature is derived from both natural and anthropogenic sources and is highly toxic. The element replaces Ca in bone structure and can result in bone degradation and cancer. Radium ($^{226}$Ra) is also the natural precursor to $^{222}$Rn, which is retained in the lungs in the form of $^{210}$Pb and $^{210}$Po.

There is a substantial body of literature reporting on GFAAS studies on the mechanism of atomization of all of the alkaline earth elements with the exception of Ra. As will be shown below, much of this information is useful when applied to ETV-ICP-MS studies. Since little published information exists on Ra, the vaporization of $^{226}$Ra compounds and its determination by ETV-ICP-MS is the focus of this paper.

Radium, as $^{226}$Ra, is currently determined largely by such techniques as alpha spectrometry,[1,2] thermal ionization mass spectrometry (TIMS),[3,4] radon emanation[5] and Cerenkov counting.[6] Recently, $^{226}$Ra has been successfully determined by inductively coupled plasma mass spectrometry (ICP-MS) using solution nebulization sample introduction[7] and electrothermal vaporization (ETV) sample introduction.[8,9] While these studies

have shown promise, no in-depth study on the vaporization of Ra or study of optimum experimental conditions for ETV determinations has been reported.

Alpha spectrometry[1,2] is the most commonly used technique for the determination of $^{226}$Ra. Sample sizes range from 1–50 ml of solution or 1–5 g of solid. The limit of detection obtained reported for alpha spectrometry[1] was $1.8 \times 10^{-4}$ Bq (0.1 fg ml$^{-1}$) for a 50 ml sample, pre-concentrated and counted for 1000 min. Using TIMS,[3,4] sample sizes can be as small as 1 g and yield detection limits of about 10 fg ml$^{-1}$. Techniques based on radon emanation[5] involve the collection of $^{222}$Rn, a decay product of $^{226}$Ra. Large sample sizes (litres) are required and ingrowth of radon takes from several days to weeks before sufficient quantities of Rn are produced for an accurate analysis. Cerenkov counting,[6] based on $\beta$-particle detection using a liquid scintillator, also requires a relatively large sample and involves a relatively long sample preparation time giving a limit of detection of 0.035 Bq l$^{-1}$ (0.95 fg ml$^{-1}$). Although all of the techniques discussed above generally offer low limits of detection for Ra, this advantage is somewhat offset by long preparation and analysis times. Preparation of liquid samples usually involves an ion-exchange separation of Ra followed by an electrodeposition preconcentration step. Each step necessarily leads to a greater possibility of contamination and/or analyte loss.

Studies on the determination of $^{226}$Ra by ICP-MS using solution nebulization[7] and ETV[8,9] sample introduction gave limits of detection of 0.2 pg ml$^{-1}$ for solution nebulization[7] and 0.27 fg ml$^{-1}$ for ETV when 50 ml of sample solution were used. These methods used either or both preconcentration by ion exchange and evaporation techniques to improve sensitivity. Analysis by ETV-ICP-MS[8] was done by drying successive samples without vaporization (multiple deposition) to increase sensitivity. This approach, however, is not suitable when sample solutions contain large quantities of dissolved salts. Alvarado and Mitchell[9] used Freon-23 as a chemical modifier and obtained a limit of detection of 0.6 fg ml$^{-1}$ for a 25 µl sample aliquot. A limit of detection of 1 fg ml$^{-1}$ was obtained without the use of Freon-23.

The use of ETV sample introduction provides an alternative means of sample introduction for ICP-MS, which serves to extend the range of application of the technique. The main advantages provided by ETV sample introduction include the use of microlitre or microgram sample sizes, the removal of matrix interferences by thermal pretreatment of the sample prior to vaporization and the ability to analyze solids, slurries and organic materials directly. Electrothermal vaporization sample introduction provides for rapid analysis in minutes compared with days or even longer for counting techniques.[5,6] As an additional advantage, many samples do not require preconcentration owing to the inherent high sensitivity of ICP-MS. In fact, in a recent paper by Smith *et al.*,[10] it was

shown that it was advantageous to use ETV-ICP-MS rather than counting techniques for the determination of all radionuclides whose half-lives were greater than about 570 years.

The purpose of this study is to elucidate the mechanism of vaporization of Ra and the other alkaline earth elements in ETV-ICP-MS and to determine the optimum measurement conditions for these elements. This work is to serve as the basis for the development of methodology for the direct determination of Ra in solids, sampled as slurries, using ETV-ICP-MS.

## EXPERIMENTAL

A Perkin-Elmer SCIEX Elan 5000a ICP mass spectrometer equipped with an HGA-600 MS electrothermal vaporizer and a Model AS-60 autosampler was used. Pyrolytic graphite coated tubes were used throughout. The experimental conditions for both the Elan 5000a and the HGA-600MS are given in Table 1.

A PTFE tube of 80 cm and 6 mm id was used to connect the HGA-600MS to the plasma torch. Optimization of the plasma and mass spectrometer was accomplished using solution nebulization, prior to switching to ETV mode. No further optimization of the ICP mass spectrometer was required with the exception of small ($\pm 50$ ml min$^{-1}$) variations in the carrier Ar flow rate. The operation of the HGA-600 MS was completely computer controlled. During the drying and pyrolysis steps of the temperature program, opposing flows of argon (300 ml min$^{-1}$) originating from both ends of the graphite tube removed water and other vapours through the dosing hole of the graphite tube. During the high-temperature or vaporization step, the dosing hole was sealed by a pneumatically activated graphite probe. Once the graphite tube was sealed, a valve located at one end of the HGA workhead directed the carrier argon gas flow, originating from the far end of the graphite tube, directly to the argon plasma at a flow rate of 800 ml min$^{-1}$.

### Standards and Reagents

High purity argon gas (99.995%, Matheson Gas Products, Ottawa, Ontario, Canada) was used. A solution of mixed alkaline earth elements was prepared by dilution of SPEX standard 1000 or 10 000 μg ml$^{-1}$ stock solutions (SPEX Industries, Edison, NJ, USA) using de-ionized water (Millipore, Mississauga, Ontario, Canada). Aliquots of all samples and

**Table 1** Instrumental operating conditions and data acquisition parameters

| | |
|---|---|
| *ICP mass spectrometer—* | |
| Rf power/W | 1000 |
| Coolant argon gas flow/l min$^{-1}$ | 15.0 |
| Auxiliary argon gas flow/ml min$^{-1}$ | 900 |
| Carrier argon gas flow/ml min$^{-1}$ | 800 |
| | |
| *HGA-600MS electrothermal vaporizer—* | |
| Sample volume/μl | 10–20 |
| Dry step | 10 s ramp |
| | 110 °C for 30 s |
| Pyrolysis step | 1 s ramp |
| | 400–2650 °C for 30 s |
| Vaporization step | 1 s ramp |
| | 900–2700 °C for 6 s |
| | |
| *Data Acquisition—* | |
| Dwell time/ms | 20 |
| Scan mode | peak hopping |
| Points/spectral peak (*m/z*) | 1 |
| Signal measurement | Integrated counts |
| Resolution | 0.7 u at 10% peak-height |

modifier solutions were 10 μl in volume. The $^{226}$Ra solution (provided by the Atomic Energy Commission of Canada, Pinawa, Manitoba) contained 5.2 Bq g$^{-1}$ of the element. The concentrated Ra stock solution was calibrated against NIST SRM 4966 (Radium-226) which was certified to contain 300 Bq g$^{-1}$ of $^{226}$Ra. NASS-3 Open Ocean Seawater reference material was obtained from the National Research Council of Canada and diluted 500-fold with deionized water prior to use as a chemical modifier or simulated sample matrix.

## RESULTS AND DISCUSSION

### Mechanism of Vaporization of Be, Mg, Ca, Sr and Ba

The mechanisms of atomization for a number of elements have been studied using GFAAS.[11–13] Sturgeon et al.[11] showed that three processes occurred leading to the production of free atoms: (1) carbon reduction of the analyte oxide followed by sublimation of the metal; (2) thermal dissociation of the oxide on the graphite surface or in the gas phase; and (3) thermal dissociation of the metal chloride. Thermogravimetric[14] and atomic absorption data[11–13] show that the oxides of the alkaline earth elements (Mg, Ca, Sr and Ba) are common intermediates, resulting from the heating (prior to vaporization) of either the chloride or nitrate form of the element.

In GFAAS, Mg oxide (MgO) and Ca oxide (CaO) vaporize from the graphite surface as oxides and in the vapour phase dissociate giving atoms.[15] Hutton et al.[16] showed by molecular emission measurements in a carbon furnace that the gaseous oxide species for Mg, Ca and Sr exist, suggesting dissociation into the elements in the vapour phase. Sturgeon et al.[11] suggested that the vapour phase composition was dependent upon the sample size; large samples produced gaseous elements directly, with thermal dissociation occurring on the surface, and small samples produced gaseous oxides before dissociating into gaseous atoms. Kantor et al.[17] supported this interpretation and Prell et al.[13] used mass spectrometry coupled with a graphite furnace to show that the oxide directly precedes the production of the analyte atoms.

There is some uncertainty surrounding the vaporization of Sr oxide. It was suggested by Moore et al.[18] that SrO(s) vaporizes to SrO(g). However, mass spectrometric studies by Porter et al.[19] suggested direct formation of the gaseous elements from the solid oxide. Nagdaev and Bukreev[20] (using a graphite rod atomizer) proposed that the most probable mechanism for free Sr and Ba atom formation is sublimation of the oxide with dissociation in the gas phase. Hutton et al.[16] obtained similar results using molecular emission measurements of SrO and Prell et al.[13] also showed that the oxide directly preceded the appearance of free Sr atoms.
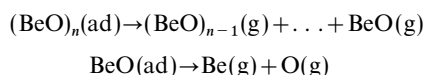
For Ba, the oxide is thought to exist predominantly in the vapour phase as a gas.[15] Jasim and Barbooti[21] suggested that free Ba is formed from the gas phase thermal dissociation of the oxide as did Nagdaev and Bukreev.[20] Frech et al.[22] used thermodynamic calculations to show that the hydroxide (gaseous and liquid) and the gaseous oxide were the precursors to gaseous Ba atom formation. Byrne et al.[23] added oxygen to the purge gas to produce signal shifts giving evidence in support of the gaseous oxide dissociation hypothesis. Prell et al.[13] showed BaO as the precursor to Ba atom formation. Sufficient vapour pressure (a few Torr) for all oxides[15] exists at their appearance temperatures to produce a signal in ETV-ICP-MS.

Beryllium has an atomization mechanism similar to the other alkaline earth elements[12] with one significant difference. For the alkaline earth elements (Mg, Ca, Sr and Ba), the species preceding the appearance of the free element has been the simple oxide, MO. Beryllium, on the other hand, forms a polymeric oxide, (BeO)$_n$ and release of the free element proceeds

as follows:

$$(BeO)_n(ad) \rightarrow (BeO)_{n-1}(g) + \ldots + BeO(g)$$

$$BeO(ad) \rightarrow Be(g) + O(g)$$

There are, however, some differences in the mode of operation of ETV-ICP-MS that may affect the usefulness of data obtained by GFAAS studies. For example, in GFAAS, during the signal measurement step (high-temperature step) no argon is flowing through the graphite tube. Production of atoms for atomic absorption can proceed by the vaporization of metal from the graphite surface to the gas phase and/or by the thermal dissociation of molecular species in the gas phase. For ETV-ICP-MS, there is a constant Ar flow of about $0.8-1$ l min$^{-1}$ through the graphite tube, which serves to remove any vaporized material (atomic or molecular) and carry it to the argon plasma where atomization and ionization takes place. For the alkaline earth elements discussed above and for both GFAAS and ETV-ICP-MS, analyte oxide is vaporized into the gas phase. This does not mean, however, that analyte signal will be observed at the same vaporization temperature for both techniques. As will be shown below, this is because, for GFAAS, the production of the analyte signal is dependent on a high enough gas phase temperature to effect thermal dissociation of the oxide, whereas, in ETV-ICP-MS, the analyte signal will result at whatever temperature the oxide is vaporized. This means that, in general, appearance temperatures (defined as the lowest temperature at which the analyte signal can be detected above baseline noise) for ETV-ICP-MS will always be lower or equal to appearance temperatures measured using GFAAS. Appearance temperatures for the alkaline earth elements measured using ETV-ICP-MS are compared in Table 2 to literature values for the appearance temperatures determined using GFAAS. Within experimental error ($\pm 100$ °C), appearance temperatures agree except for Ba for which the ETV-ICP-MS temperature is significantly lower. This lower temperature may be attributable to the higher sensitivity of ICP-MS compared with GFAAS. There is no reported value for the appearance temperature for Ra using GFAAS.

## Mechanism of Vaporization of Ra

Radium is the heaviest of the alkaline earth elements and shares many chemical properties with the rest of the group, particularly Ba. When the alkaline earth elements are discussed as a group, Be and Mg are usually kept separate because they exhibit different chemistries than the rest of the group.[24] Calcium, Sr and Ba are usually classed together, with Ra often paired to Ba.

Radium compounds follow the general solubility trends for the alkaline earths (sulfate solubility decreases and hydroxide solubility increases as atomic number increases, *etc.*) except for the nitrate, which is slightly more soluble than the Ba compound. Thermogravimetric analysis of radium nitrate and carbonate[25] have revealed the existence of several phases of an oxide, believed to be RaO, at temperatures as low as 300 °C

and as high as 1230 °C. Thermochemical properties of the alkaline earth elements follow well defined trends[26] and much of the information available on Ra is currently derived from these trends. Few experimental measurements of the thermodynamic properties of RaO have been completed owing to its high reactivity.[25] Radium oxide (RaO) is a highly aggressive substance that readily attacks crucible and calorimeter materials and, to date, no definite material has been conclusively identified for which the formula RaO can be assigned.[25]

In ETV-ICP-MS, it is often observed that for many substances there is sufficient vapour pressure (several Torr) at the melting point to give rise to a signal. Radium oxide was calculated to melt at 1615 °C.[27] This temperature is (within error) the same as the appearance temperature (1600 °C) for Ra obtained from the vaporization of both the nitrate and chloride form. This supports the possibility that the oxide is the most likely form of Ra vaporized at the appearance temperature.

As shown above, all the alkaline earth elements most probably volatilize as oxides. The chemical and thermodynamic similarities between Ra and the other alkaline earth elements, the appearance temperature for Ra in ETV-ICP-MS and its similarity to the melting point of Ra oxide suggest a likely mechanism of vaporization. The evidence provided above is incomplete and perhaps circumstantial, but, in the absence of more quantitative data, a reasonable mechanism for the production of the Ra signal at the appearance temperature in the ETV is vaporization of RaO(s) to RaO(g) which is then transported to the argon plasma where atomization and ionization take place.

## Optimization of Experimental Conditions

A typical ETV heating program contains at least three steps. A low temperature step ranging from 80 to 110 °C is used to remove solvent and volatiles not containing the analyte. A second step, generally called the pyrolysis step, is used to remove selected matrix components and/or to activate chemical modifiers. The third step is the high temperature or vaporization step which is used to vaporize the analyte. It is during this step that ICP-MS data are collected. The temperature and the rate of heating of the drying step are normally determined experimentally and are usually dependent on the nature of the sample matrix. The maximum pyrolysis temperature that can be used is the temperature at which the analyte is lost in significant quantities. In order to measure the maximum allowable pyrolysis temperature for the alkaline earth elements, a curve was constructed of the analyte signal obtained at different temperatures for a 30 s (1 s ramp time) pyrolysis step. In each case, the same vaporization temperature (2500 °C) was used throughout. Increasing the hold time for the pyrolysis step generally decreased the temperature at which analyte losses were detected. The 30 s hold time selected for this study is reasonable based on typical heating programs used for the analysis of real samples. The pyrolysis and vaporization curves for Ra are shown in Fig. 1. These data show that losses begin to occur at a pyrolysis temperature of around 1400 °C for Ra. Fig. 2 shows pyrolysis curves for the other alkaline earth elements. The pyrolysis temperatures obtained for these elements (Table 3) are generally lower by several hundred degrees than those reported in GFAAS studies. This may be due to the much smaller quantities of analyte vaporized in ETV-ICP-MS (fg–pg) compared with GFAAS (ng–µg).[32] As shown in Fig. 2, Be losses occurred at relatively low temperatures. This may result from the low temperature vaporization of Be compounds such as Be(NO$_3$)$_2$ (bp 142 °C) or BeCl$_2$ (bp 520 °C) depending upon the acid used in solution. Maessen *et al.*[33] reported that approximately 10% of the Be is lost from the furnace due to diffusional losses before the free atom signal

**Table 2** Appearance temperatures for the alkaline earth elements

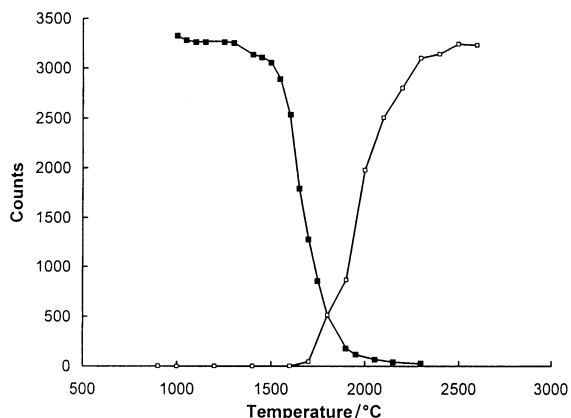| Element | Appearance temperature/°C | | |
| | GFAAS | ETV-ICP-MS | Reference |
| --- | --- | --- | --- |
| Be | 1227 | 1200 | 11 |
| Mg | 1237 | 1200 | 10 |
| Ca | 1577 | 1500 | 10 |
| Sr | 1367 | 1300 | 13 |
| Ba | 1727 | 1500 | 21 |
| Ra | — | 1600 | this work |

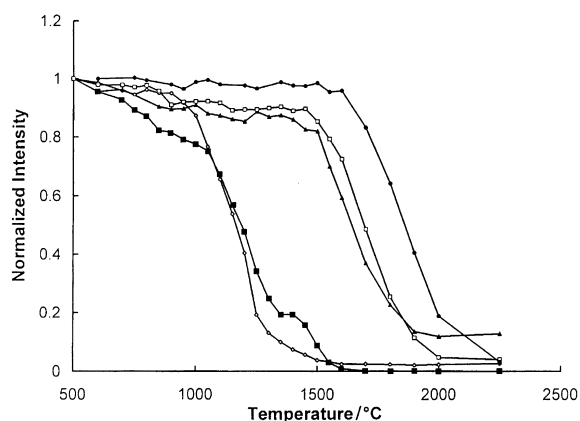**Fig. 1** Pyrolysis (■) and vaporization (□) curves for 0.25 pg Ra.



**Fig. 2** Pyrolysis curves of the alkaline earth elements in ETV-ICP-MS (vaporization 2600 °C): Be (■), Mg (◇), Ca (▲), Sr (□), and Ba (●).

**Table 3** Pyrolysis temperatures for the alkaline earth elements

| | Pyrolysis temperature/°C | | |
|---|---|---|---|
| Element | GFAAS | ETV-ICP-MS | Reference |
| Be | 900 | 500 | 28 |
| Mg | 900 | 900 | 29 |
| Ca | 1200 | 700 | 30 |
| Sr | 1500 | 800 | 31 |
| Ba | 1500 | 1500 | 30 |
| Ra | — | 1400 | this work |

is observed in GFAAS. Vanhoe et al.[28] reported loss of Be at 900 °C in GFAAS when no modifier was used. Meah[34] also recorded Be losses at very low temperatures when vaporized in the presence of acids and salt matrices. Thus if all alkaline earth elements were to be determined as a group by ETV-ICP-MS, a pyrolysis temperature of 700 °C or less should be used to prevent losses of the more volatile Be. However, with the use of magnesium nitrate as a chemical modifier, Be can be stabilized to a temperature of 1500 °C.

A second set of experiments exploring the relationship between the vaporization temperature and the integrated signal for the alkaline earth elements showed that the maximum signal was obtained at a vaporization temperature of 2500 °C or greater when a 500 °C pyrolysis step was used. As an example, the vaporization curve for Ra is given in Fig. 1. Using these vaporization conditions completely removes the analyte from the surface of the graphite tube with no memory effects observed.

## Analytical Figures of Merit

Analytical figures of merit for the determination of $^{226}$Ra by ETV-ICP-MS are given in Table 4. The limit of detection for Ra was calculated as the mass of Ra equivalent to a signal equal to three times the standard deviation of the blank. An absolute limit of detection of 1.7 fg was obtained, which corresponds to a relative limit of detection of 34 fg ml$^{-1}$ in a 50 μl sample. The analyte signal could be measured with a precision of 3.9% and 5.3% for integrated and peak-height signal measurements, respectively.

## Effect of Physical Carrier and Signal Suppression Due to Matrix Components

The effect of using physical carriers to improve analyte transport from the graphite tube to the argon plasma was shown by Hughes et al.[35] In this study, the use of NASS-3 (reference seawater diluted 500 times) was shown to be an effective physical carrier for many elements resulting in signal enhancements of up to a factor of ten. The effects of NASS-3 seawater on the Ra signal (Table 5) was studied by adding 10 μl of solutions containing increasing concentrations of NASS-3 to a 10 μl aliquot of sample solution containing 0.1 ng ml$^{-1}$ Ra. Pyrolysis and vaporization temperatures of 700 and 2500 °C, respectively, were used. A seawater matrix can also be used to determine the effect of added matrix components on possible signal suppression.

When small quantities of salt were added, the Ra signal was enhanced by up to 30%. Upon adding greater quantities of salt, the signal was suppressed by as much as 75% when 360 μg of salt were added. Radium is present in seawater at $8.9 \times 10^{-11}$ μg ml$^{-1}$ (ref. 36) corresponding to $8.9 \times 10^{-4}$ fg in a standard 10 μl sample. This quantity of $^{226}$Ra is well below the observed ETV-ICP-MS limit of detection for Ra (1.7 fg) and will not affect the observed signal in experiments using seawater as a modifier.

As was reported by Hughes et al.[35] the initial enhancement effect is probably due to an increased transport efficiency, while, at higher added salt masses, signal suppression occurs. The modest enhancement observed for Ra when small quantit-

**Table 4** Analytical figures of merit for Ra

| Blank— | Integrated Signal | Peak height |
|---|---|---|
| $^{226}$Ra | 53 | 94 |
| σ, n = 10 | 8 | 16 |
| RSD (%) | 15 | 17 |
| 3σ | 24 | 49 |
| | | |
| Radium— | | |
| $^{226}$Ra (1.4 pg) | 19 600 | 36 737 |
| σ, n = 5 | 760 | 1959 |
| RSD (%) | 3.9 | 5.3 |
| LOD (abs) fg | 1.7 | 1.7 |
| LOD (rel) (50 μl)/fg ml$^{-1}$ | 34 | 34 |
| LOD/Bq g$^{-1}$ | $1.3 \times 10^{-3}$ | $1.3 \times 10^{-3}$ |

**Table 5** Effect of added salt on Ra signal

| Amount of salt/μg | Enhancement* |
|---|---|
| 0 | 1.00 |
| 0.72 | 1.32 |
| 3.6 | 1.29 |
| 7.2 | 1.12 |
| 36 | 0.78 |
| 72 | 0.61 |
| 360 | 0.25 |

* Defined as the ratio of the signal obtained when Ra is vaporized with salt divided by the Ra signal obtained when vaporized alone.
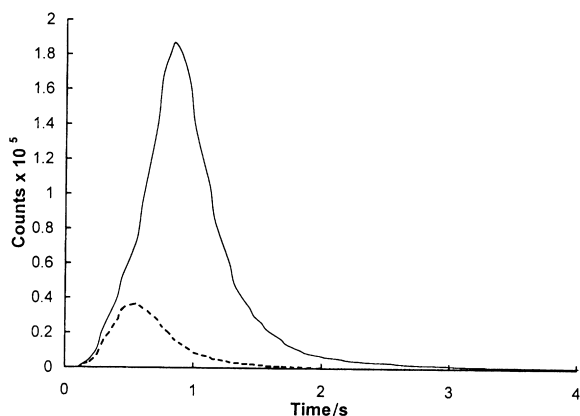
**Fig. 3** ETV-ICP-MS signals for Ra (- - -) and Ba (——).

ies of salt were added may be due to the presence of Ba in solution with Ra which itself acts as a physical carrier. The Ra standard used, as well as the NIST material, contained Ba which served as a carrier during the Ra purification step. Both Ra and Ba are co-volatilized during the vaporization step as shown in Fig. 3.

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