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Determining Gallium from Plutonium Using Anion Exchange and X-Ray Fluorescence

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DETERMINING GALLIUM FROM PLUTONIUM USING ANION EXCHANGE AND X-RAY FLUORESCENCE

by

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ABSTRACT

Gallium in plutonium is determined using anion exchange and x-ray fluorescence. A 6M HCl solution of plutonium, with ascorbic acid added, is passed through an anion exchange resin column. This process sticks the gallium to the resin and allows the plutonium to pass through the column. Zinc, as an internal standard, is pipetted into an empty beaker into which the gallium is eluted with 0.02M HCl. This solution is then evaporated to approximately 2 mL and is transferred to a 10-mL volumetric flask. The solution is poured into an x-ray cell, and the Kα line for both gallium and zinc are read on the x-ray instrument. We then compare the ratio of the intensities for gallium and zinc from a sample with that from standards. The relative standard deviation for the range 0.2% to 1% gallium is 0.36%.

INTRODUCTION

A method to determine gallium in plutonium was desired to replace a spectrophotometric procedure using an oxine-chloroform extraction.[1] Because gallium adsorbs to anion exchange resin better than any another element in the periodic chart,[2] we used anion-exchange coupled with x-ray fluorescence to determine gallium in plutonium. Because gallium has a Kα line with an energy of 9.2 KeV, it is an optimal element for x-ray analysis.

To achieve the best precision possible, we chose zinc as our internal standard. Although zinc will adsorb out of 6M HCl, it does not adsorb as well as gallium and elutes at a different rate than gallium. We, therefore, add the zinc to the system after the gallium has been separated from the plutonium.

Equipment and Reagents

In this work, we use the following equipment:

- Aluminum cell holder, 50-mm o.d.
- Columns, glass, ion-exchange, 19 by 200 mm
- Mylar film, 6- μm thick
- Sample cells, x-ray, Chemplex, plastic, series 1400, 32-mm o.d.
- X-ray spectrometer; Siemens SRS 300 microprocessor-controlled sequential x-ray spectrometer system; rhodium-target x-ray tube

We also used the following reagents:

- Gallium solution, 10.0000 mg/mL, from 99.99% gallium metal
- Gallium solution, 1.0000 mg/mL
- Zinc solution, 5.00 mg/mL
- Ascorbic acid, Eastman Organic Chemicals, L-ascorbic acid
- Hydrochloric acid, 6M, 0.02M
- Ion-exchange resin, analytical grade anion exchange resin, AG 1 x 4, 50 to 100 mesh, chloride form, Bio-Rad Laboratories

PROCEDURE

1. Dissolve 500 mg of plutonium metal in a covered 20-mL beaker with 1 mL of 12M HCl. The resulting solution is 6M HCl.
2. Rinse cover and beaker with 6M HCl and add 100 mg ascorbic acid to beaker to ensure that all the plutonium is Pu^{+3}.
3. Condition anion exchange column with 6M HCl three times.

4. Add the 6M HCl-plutonium solution to the anion exchange column. Rinse the beaker with 6M HCl and add to the column. Continue rinsing and adding to the column until 40 mL of HCl has passed through the column.
5. Pipet 2 mL of the 5.00 mg/mL zinc solution into 20-mL beaker. Then elute the gallium off the column into this beaker with 0.02M HCl.
6. Evaporate the gallium and zinc solution to approximately 2 mL and transfer the solution to a 10-mL volumetric flask.
7. Prepare a "cold" place inside the "hot" box using paper towels.
8. Transfer the sample solution from the 10-mL volumetric flask to an x-ray cell, being careful to keep the exterior of the cell uncontaminated.
9. Cover the cell with Mylar film. Check for leaks by turning the Mylar side of the cell down, wait briefly, then look for leaks. Do this just before placing the cell in the spectrometer.
10. Place the covered x-ray cell containing the sample solution in an aluminum cell holder that also has a Mylar cover.
11. Excite the sample solution with a rhodium-target x-ray tube. Measure the following 2θ settings for 60 s for gallium and 30 s for zinc:

2θ	Measurement
38.92	Ga Kα
40.20	Background 1
40.20	Background 2
41.81	Zn Kα

We analyze the sample with the spectrometric parameters shown in Table I.

Figure 1 shows a plot of intensity vs 2θ for gallium and zinc after separation from 500 mg of plutonium by anion exchange. The intensity of the gallium is 4800 c/s.

Table I. X-Ray Operating Parameters

X-ray tube	rhodium
Voltage	60 kV
Current	50 mA
Counters	Scintillation and Flow
Analyzing crystal	LiF 200
Soller slit	Fine
Counting time	60 s Ga
Counting time	30 s Zn

STANDARDS

The standards contain known amounts of gallium and zinc as listed below:

Standard No.	Gallium (mg)	Zinc (mg)	Plutonium (mg)
Ga-1	0.000	10.00	500
Ga-2	0.000	10.00	500
Ga-3	3.000	10.00	500
Ga-4	3.000	10.00	500
Ga-5	5.000	10.00	500
Ga-6	5.000	10.00	500

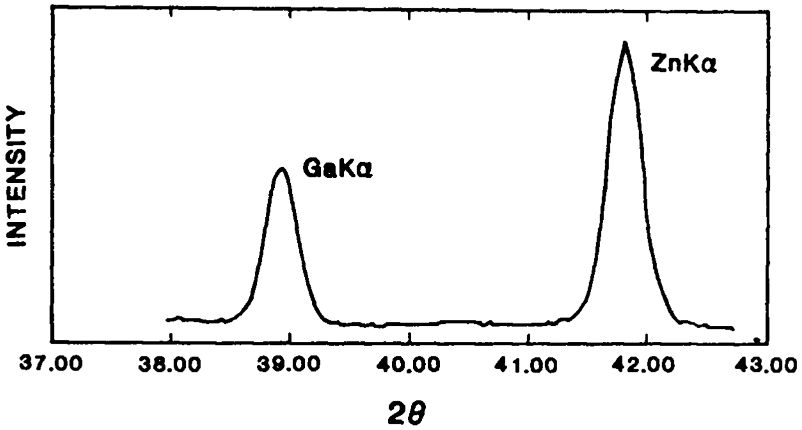

Fig. 1. Wavelength scan for gallium and zinc.

We pipet the appropriate amounts of the gallium solution into each of the beakers and add the plutonium solution to each beaker. We then analyze the standards as described in the "Procedure" section. Figure 2 shows a plot of intensity ratios (Ga/Zn) vs concentration of gallium.

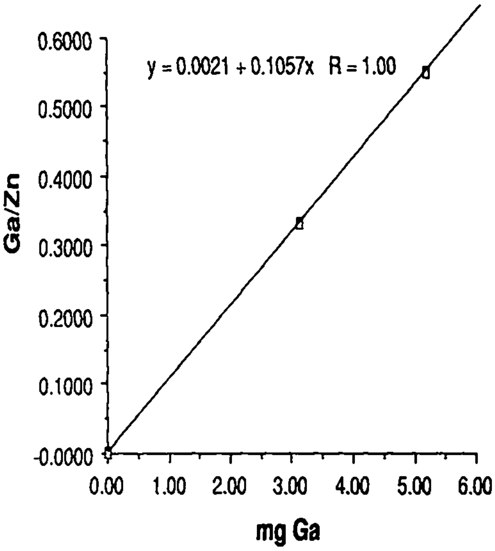

Fig. 2. Plot of intensity ratios (Ga/Zn) vs concentration of gallium.

CALCULATIONS

The Siemens spectrometer gives the net intensity values. To obtain the Ga/Zn ratios, we divide the gallium counts per second by the zinc counts per second. We do a least squares fit for the standards, relating Ga/Zn ratios to the gallium concentrations. To calculate the concentration of gallium in the analyzed samples, we use the coefficients for the equation representing this standard curve.

INTRALABORATORY EXCHANGE

In the course of this work, we conducted an intralaboratory exchange program (round raven sample exchange) of four samples containing various amounts of gallium. These four unknown (to the analysts) samples were distributed to six laboratories in the Analytical Chemistry Group (CLS-1) that use different analytical techniques. Each technique employed an instrument for measurement after a separation had been achieved by a chemical procedure. Table II shows the analytical techniques with the instrumentation and chemical separation used.

Table II. Analytical Techniques Used in Round Raven Exchange

Instrumentation	Chemical Separation
Mass Spectroscopy	Anion Exchange
X-Ray Fluorescence	Anion Exchange
X-Ray Fluorescence	None (Direct Reading in Pu)
Direct Current Plasma	Tributyl Phosphate Extraction
Inductively Coupled Plasma	Tributyl Phosphate Extraction
Spectrophotometry	Oxine-Chloroform Extraction

The "unknown" plutonium solutions are shown in Table III.

Table III. Concentration of Gallium in Plutonium Solutions

Sample	% Gallium
Solution A	0.6205
Solution B	0.7790
Solution C	0.7790
Solution D	1.000 ± 0.02

Solutions A, B, and C were prepared by aliquoting a large volume of a carefully and accurately prepared gallium solution into a volumetric flask to which plutonium was added. Solution D was a well-characterized Rocky Flats exchange metal. The ± for Solution D indicates a little more uncertainty than the other solutions.

Solution B is a high-purity solution of plutonium and gallium, whereas Solution C has the same concentration of gallium but has a relatively high impurity level. Table IV shows the impurity content of Solution C.

Table IV. Impurity Content of Solution C

Element	Impurity Level
Aluminum	750
Americium	1800
Chromium	150
Iron	400
Nickel	200
Neptunium	100
Uranium	400

We compared the impurity levels because earlier work by

CLS-1 on United Kingdom (UK) exchange samples indicated that a high impurity level might cause difficulty in obtaining good agreement with the UK for gallium. A little later in this report, we shall see if that is true for these samples. A complete tabulation of all the results for the four samples by the six methods is given in Table V.

We also display this data in the following graphics. This graphic method is known as the double-sample, graphic analysis method as described by W. J. Youden.[3,4] An example of such a graphic analysis display is shown in Fig. 3.

The information shown in Fig. 3 is also complex, so we wish to explain from the beginning how the double-sample, graphic analysis method is used. If we look at Fig. 4, we see that a concentration range for Solution A has been put on the Y axis, and similarly a concentration range for Solution B has been put on the X axis. The values of gallium for Solutions A and B provide the two coordinates to plot the one point for the true gallium values for the two solutions.

If the six analytical methods were very accurate and very precise, the points plotted for each of them would fit precisely on top of the plot for the standard values for the two solutions. We know, however, that this is highly unlikely. If the six methods were subject only to random errors, the plotted points should scatter about the true point into each of the four quadrants.

In Fig. 5, we add the two median lines that go exactly through the standard point to form four quadrants.

In Fig. 6, we selected one of the six methods, ICP, and used the two values obtained from the solutions by the ICP method to

Table V. Statistics for the Four Solutions by the Six Methods

Method		Soln. A	Soln. B	Soln. C	Soln. D
Mass Spec.	x, % =	0.617	0.777	0.777	1.002
	n =	4	4	4	2
	% RSD =	0.25	0.28	0.29	0.15
XRF-IE	x, % =	0.612	0.774	0.778	0.984
	n =	6	6	6	6
	% RSD =	0.39	0.40	0.21	0.41
XRF-Dir.	x, % =	0.618	0.771	0.785	0.999
	n =	4	4	4	4
	% RSD =	2.36	0.85	1.79	1.33
DCP	x, % =	0.601	0.734	0.724	0.827
	n =	4	4	4	4
	% RSD =	3.04	1.26	2.23	1.45
ICP	x, % =	0.652	0.811	0.821	1.0
	n =	1	1	1	1
Oxine	x, % =	0.613	0.770	0.779	1.00
	n =	5	5	5	4
	% RSD =	0.55	0.44	0.39	0.40
True Value	x, % =	0.6205	0.779	0.779	1.00 ± 0.02

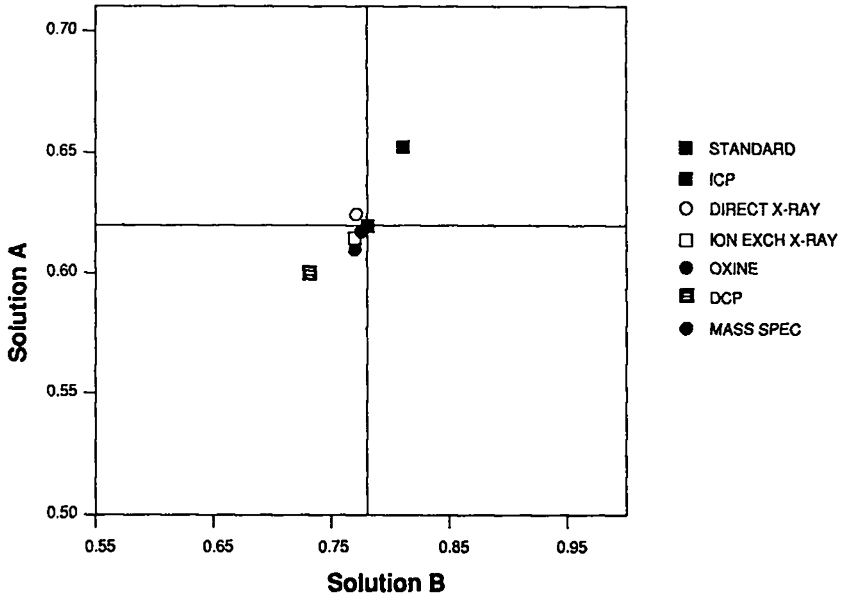

Fig. 3. Solutions A and B showing gallium results from all methods.

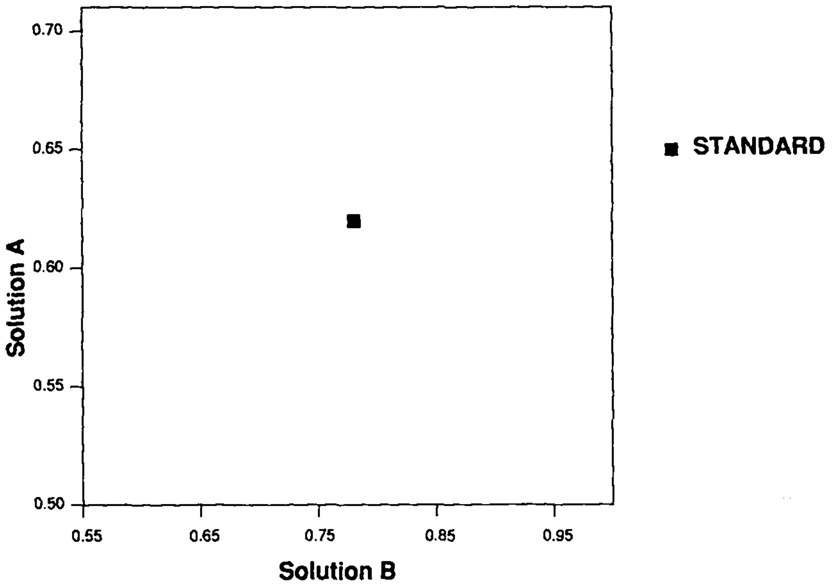

Fig. 4. Solutions A and B showing standard gallium results.

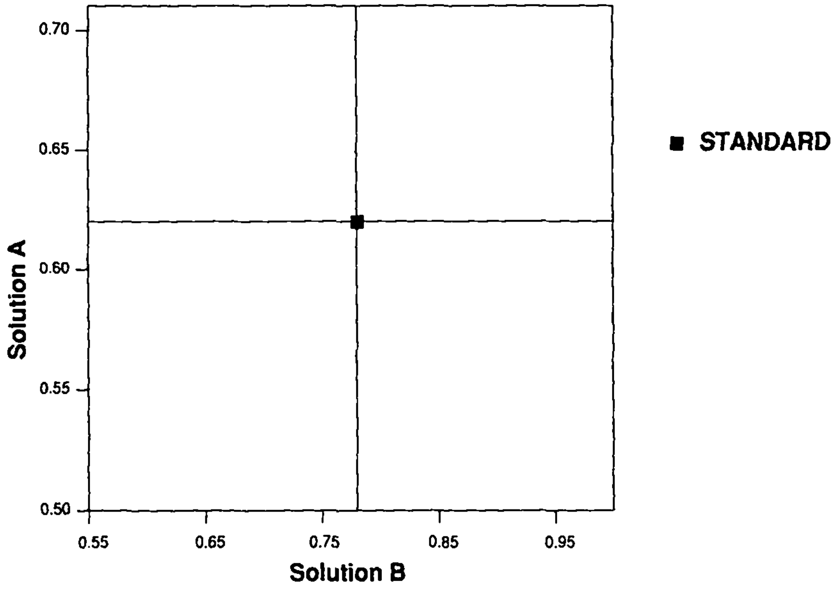

Fig. 5. Solutions A and B with median lines.

plot the point representing ICP. We see that whatever errors are involved here have put this point in the upper right quadrant.

In Fig. 7, we have added the point provided by the results obtained from the direct x-ray method; this point falls into the upper left quadrant.

The addition of the third analytical point, from the x-ray fluorescence-ion exchange (XRF-IE) method, gives us a point that falls in the lower left quadrant (Fig. 8).

In Fig. 9, we have added the results from the remaining three analytical methods. Note that the random distribution of the points around the standard point has not continued and that now each method has a slight bias, causing results to be either high in both samples or low in both samples.

In Fig. 10, we have a new combination of solutions; results from Solution A are plotted against results from Solution C. We see a similar spread of results with the same methods distributed in the same relationship to each other.

Figure 11 shows a comparison of results from Solutions A and D. Again, we see a distribution of the six methods similar to the other graphic analyses.

An interesting comparison is that of results from Solutions B and C. These two solutions have the same concentration of gallium but differ in the amount of impurities. Solution C has the impurities shown in Table IV, and Solution B is a high-purity plutonium with only gallium in it.

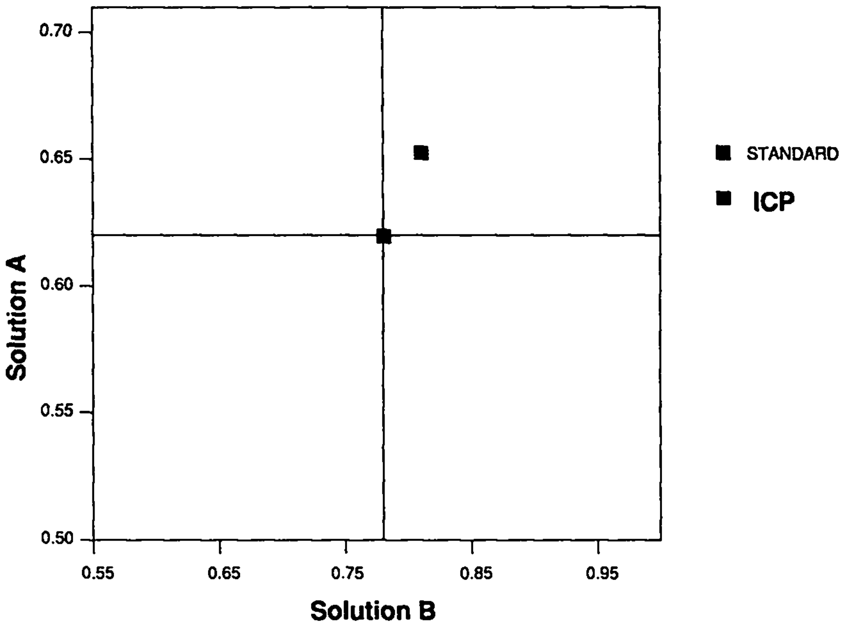

Fig. 6. Solutions A and B adding gallium results from ICP.

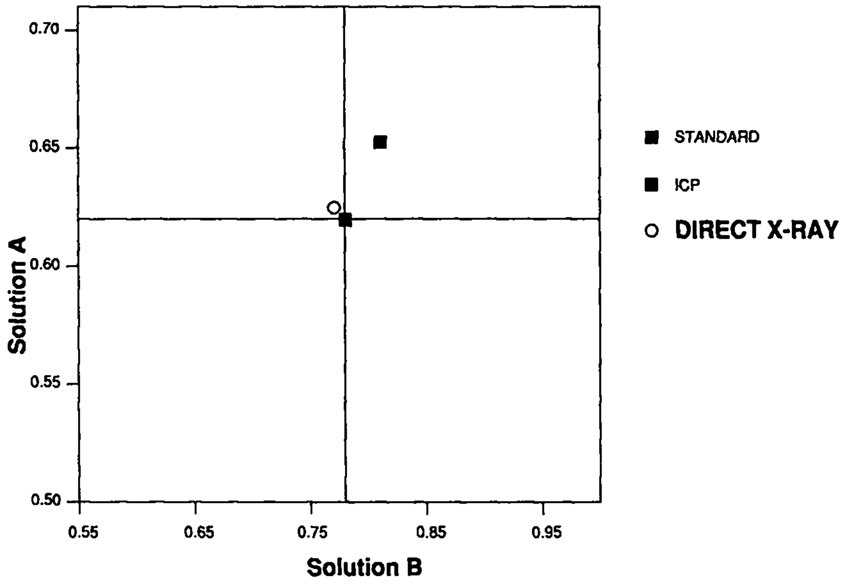

Fig. 7. Solutions A and B adding gallium results from direct x-ray.

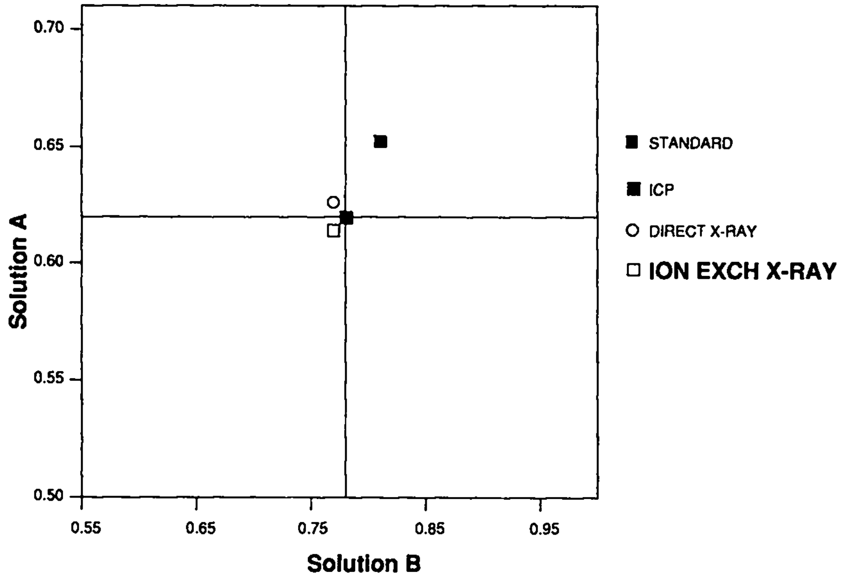

Fig. 8. Solutions A and B adding gallium results from ion-exchange x-ray.

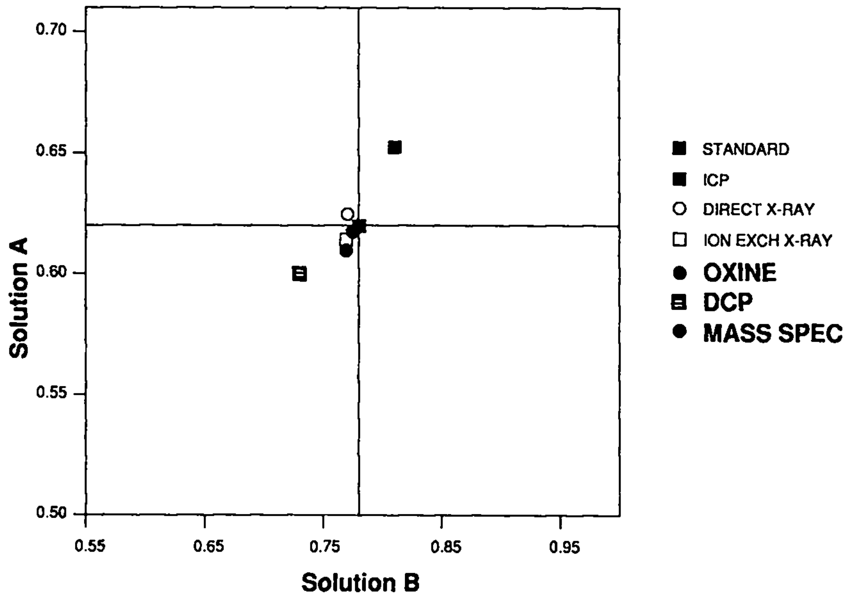

Fig. 9. Solutions A and B showing gallium results from all methods.

Figure 12 shows a plot of the results for Solution B versus those for Solution C. The six methods have the same pattern as in the other graphs. The question of the impact of the impurities asked earlier can now be answered.

A comparison of the results from Solution B versus Solution C is shown in Table VI. A T-test showed that there was no difference between the results obtained for Solution B and those obtained for Solution C.

Figure 13 shows an enlarged scale for a better view of the closely grouped points shown in Fig. 12.

Table VI. Comparison of Results of Solutions B and C

Soln. B	Soln. C
0.777	0.777
0.774	0.778
0.771	0.785
0.734	0.724
0.811	0.821
0.770	0.779
x = 0.7728	x = 0.7773
σ = 0.0245	σ = 0.0310
%RSD = 3.167	%RSD = 3.991

T-Test D.F. = 10 T = 0.279

Critical Value (99%) = 3.169
Critical Value (95%) = 2.228

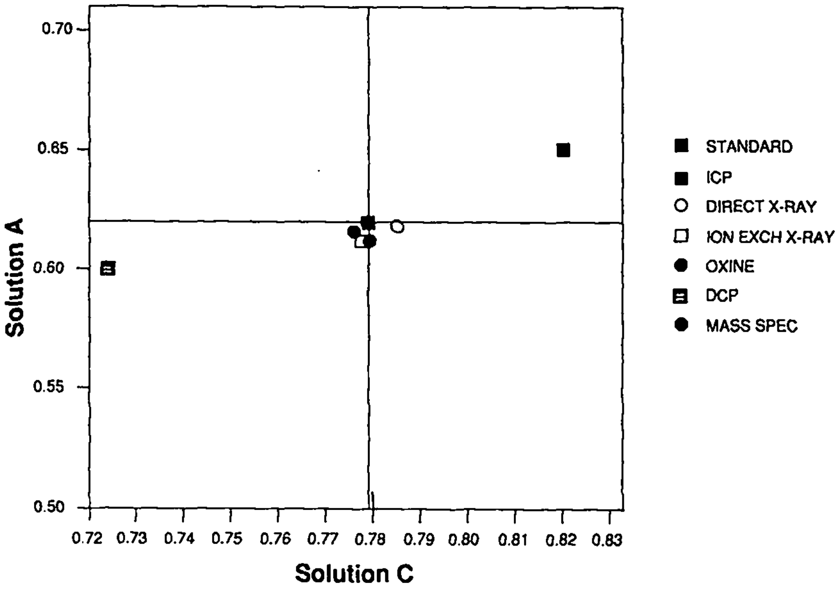

Fig. 10. Gallium results from Solutions A and C.

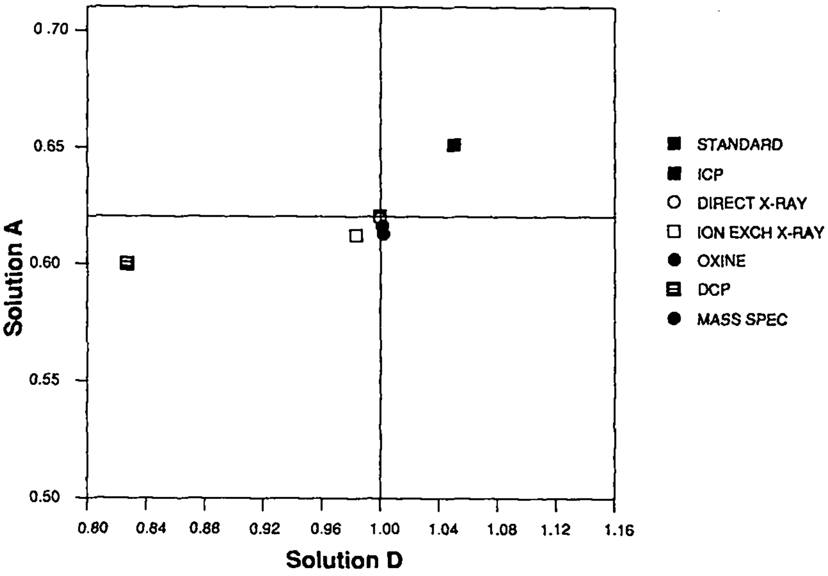

Fig. 11. Gallium results from Solutions A and D.

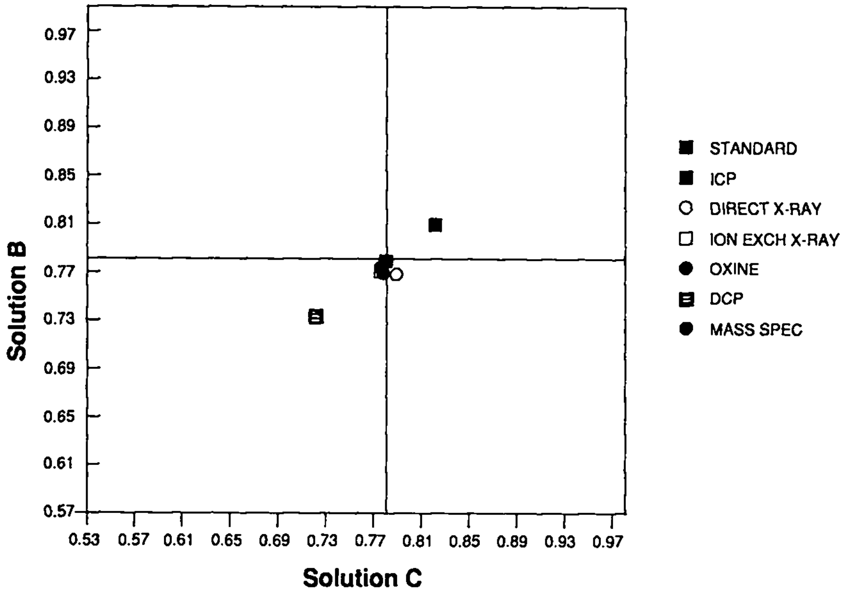

Fig. 12. Gallium results from Solutions B and C.

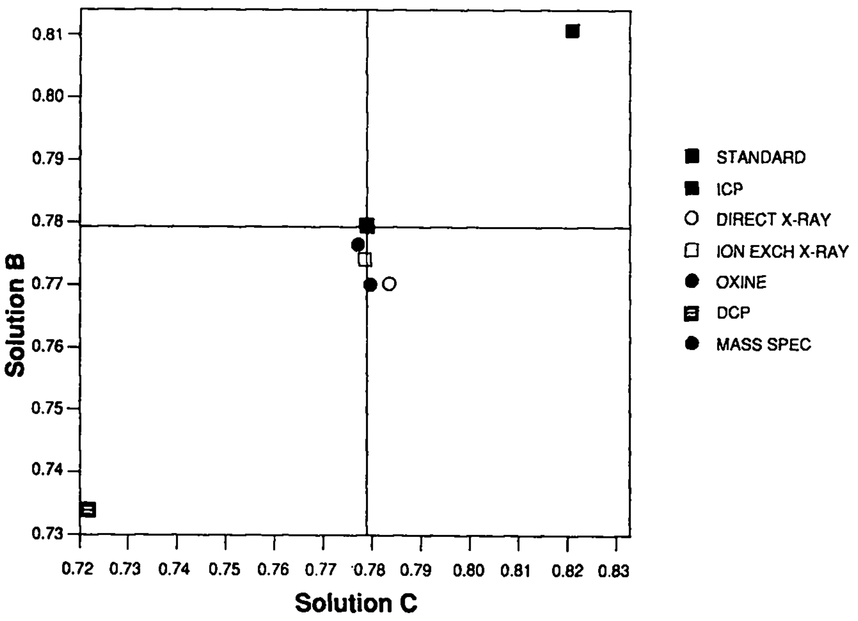

Fig. 13. Solutions B and C in an enlarged scale.

Figures 14 and 15 show the comparison between Solutions D and C and Solutions D and B, respectively.

The important part of this study is to determine which method is the best with regard to both accuracy and precision. Table VII lists accuracy and precision values for the methods.

To determine the best method, we devised a ranking system. By subtracting the accuracy for each method from 100 and adding the absolute value of that result to the RSD, we should have a value that ranks the methods for both accuracy and precision. In Table VIII, we rank the top four methods.

TABLE VII. Accuracy and Precision of Methods

Method	%Accuracy
XRF-Direct	99.81
Mass Spec	99.78
XRF-IE	99.07
Oxine	101.10
ICP	104.93
DCP	91.68

Method	%RSD
Mass Spec	0.24
XRF-IE	0.30
Oxine	0.45
XRF-Direct	1.58
DCP	2.00
ICP	---[a]

[a] Only one result obtained by this method.

Table VIII. Combined Ranking of Methods

Method	Ranking Sum
Mass Spec	0.46
XRF-AE	1.23
Oxine	1.55
XRF-Direct	1.77

XRF-Direct has an unacceptably high precision because it is considerably worse than that for Oxine, which is the method being replaced. XRF-IE and Mass Spec are acceptable methods with Mass Spec being the best and XRF-IE next. We, of course, are working with XRF-IE, the method detailed in this report. The range of relative standard deviations for the XRF-IE method, determined on the four samples previously discussed plus one additional sample at 0.18% gallium, is shown in Table IX.

Table IX. Precision for XRF-IE

Sample	Gallium Conc. (%)	RSD (%)
Sample 1	0.18	0.40
Solution A	0.62	0.39
Solution B	0.78	0.40
Solution C	0.78	0.21
Solution D	1.00	0.41
		Av = 0.36

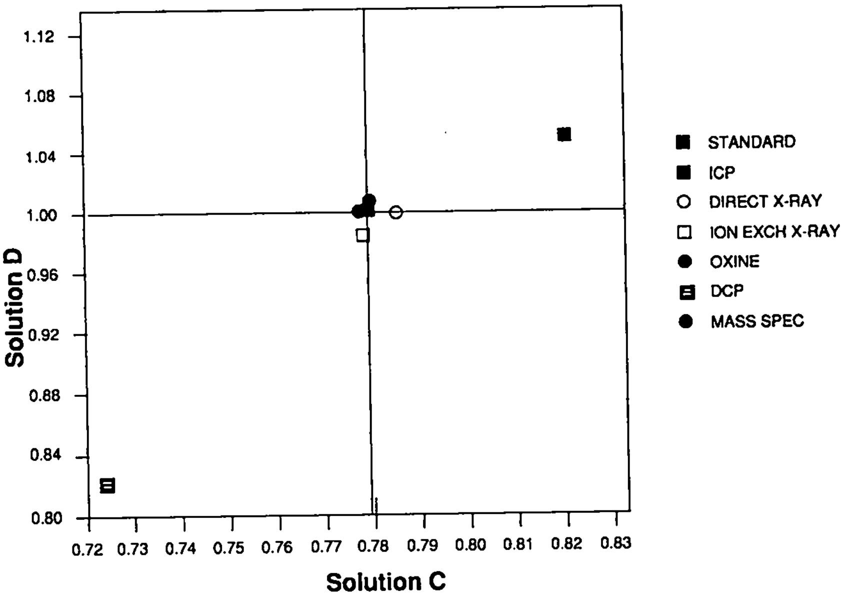

Fig. 14. Gallium results from Solutions C and D.

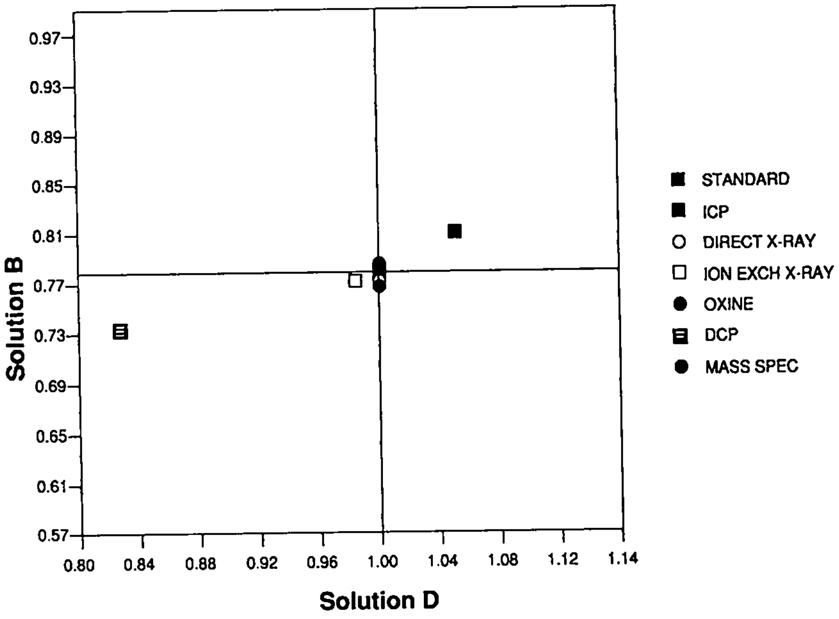

Fig. 15. Gallium results from Solutions B and D.

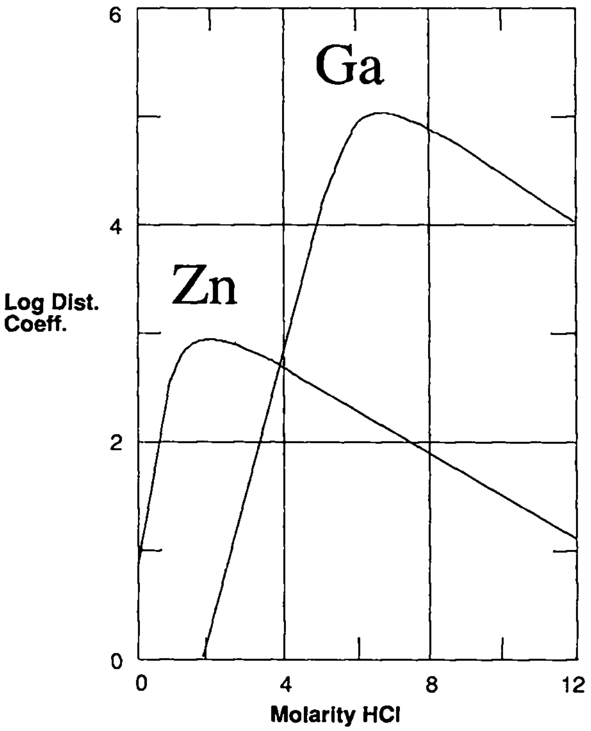

Fig. 16. Adsorption curves for gallium and zinc.

DISCUSSION

Figure 16 shows the sorption curves for both zinc and gallium on anion-exchange resin. In a test, we adsorbed both zinc and gallium on an anion exchange resin column with 6M HCl and then eluted with 20 mL of 0.1M HCl. The eluate solution was analyzed, and we discovered that only the gallium had come off the column. We then eluted with an additional 20 mL of 0.1M HCl. This solution was analyzed, and we found large amounts of zinc.

The first 20 mL of 0.1M HCl eluted the gallium off the column. In the process, the molarity of the HCl on the resin (see Fig. 16) was lowered, thus causing the zinc to be retained even better than at 6M HCl. The second 20 mL of 0.1M HCl was able to lower the molarity to nearly zero so that the zinc was freed from the resin. A scan of this second solution, however, revealed that a small amount of gallium had been retained with the zinc after the first elution and had come off with the zinc in the second elution. Figure 17 is the scan of this second solution and shows a gallium peak present.

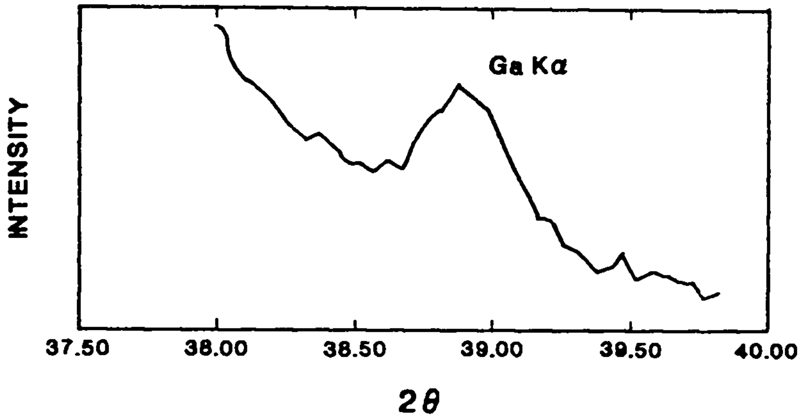

Fig. 17. Scan of gallium in second solution.

In view of this small but significant amount of gallium remaining on the column, we decided that an eluant solution of lower molarity should probably be used. We ran an experiment to test the 0.1M HCl against a 0.02M HCl solution, using four samples each of a 0.18% gallium in plutonium solution. The results are shown in Table X.

We see from Table X that 0.02M HCl gives significantly higher gallium results than does 0.1M HCl as an eluant. Therefore, the molarity of the HCl used in this procedure should be 0.02M.

Table X. Eluant Comparison of 0.02M HCl vs 0.1M HCl

0.02M	0.1M
x = 0.1774	x = 0.1675
σ = 0.0008	σ = 0.0008
RSD = 0.45%	RSD = 0.48%
T Test:	T = 14.55
Critical Value (99%)	3.707

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