

An Application of Factor Analysis for the Analysis of Osmium and Ruthenium by Neutron Activation Analysis

Jae Ung Choi, Kwon Soo Chun, Jong Du Lee[†], Chul Lee, and Koo Soon Chung[‡]

Department of Chemistry, Hyanyang University

[†]Korea Atomic Energy Research Institute

[‡]Department of Chemistry, Sogang University, Seoul 121-742

Received December 21, 1992

Factor analysis was applied to evaluate the multivariate data of gamma-ray spectra. For this purpose, mixed gamma-ray spectra of the two elements (Os and Ru) were obtained from the four ancient coins through radiochemical distillation and counting. The spectra obtained were combined with five standard spectra to produce a data matrix (900×9). AFA (abstract factor analysis) was applied to the data matrix and two factors were found to be Os and Ru. The Os and Ru contents in the coins were then determined by means of TTFA (target transformation factor analysis). The results showed that TTFA could give more accurate data as compared to the conventional method using one or two gamma ray peaks. Various detection limits, i.e., critical, detection, quantitative limit, were calculated using the method suggested by Currie and the results showed that TTFA is ten times more sensitive than that obtained by the method using one characteristic peak.

Introduction

In the analysis of the platinum group metals (PGM), the tetroxides of both osmium and ruthenium are collectively distilled. The distillation procedure including the oxidizing agents and the receiving solutions for these tetroxides was proposed by one of the present authors.¹

After the simultaneous distillation, each element was radiochemically determined by measuring the photopeak area of ¹⁹¹Os and ¹⁰³Ru at 45 and 498 KeV, respectively.¹ In this method, one photopeak area was measured for the determination of each element. This is a univariate approach to analysis. In this method, only one photopeak among the many peaks obtained from the spectra is selected and used to calculate the amounts of each element. This approach has been used in the neutron activation analysis (NAA). Therefore the most suitable peak should be carefully selected to reduce the counting error and the background produced from the Compton scattering. Unfortunately there is no obvious criterion to select the peak. Accordingly the peak which has high counting rate with no interference from other peaks and the Compton continuum is generally chosen for analysis. However, using this approach, much potentially useful information encoded in the other small peaks and the Compton continuum are ignored.

These problems could be circumvented if a multivariate approach is used, in which all the spectra data are used. Multivariate analysis has been used in many areas, with each using a different nomenclature. One of the most commonly applied branches is factor analysis (FA). Target transformation factor analysis (TTFA),¹ which is one branch of FA, has been applied successfully in IR spectrometry² and in inductively coupled optical emission spectrometry.³ TTFA has also been proposed in the spectrum analysis for the NAA.⁴

In the present investigation, abstract factor analysis (AFA), which is also one branch of FA, has been used to determine the number of factors. Thereafter, TTFA has been used to determine the degree to which each factor contributes to the spectra of the coin samples. By this method, the mixed

gamma-ray spectra of two distilled platinum group metals (Os and Ru) have been analyzed to determine the contents of these two metals in the ancient coins.

Experimental

Sampling. The surfaces of the ancient Korean coins, the Choson "Sangpyong Tongbo", which were obtained from the National Research Institute of Cultural Properties, Seoul, Korea, were cleaned by air brushing, washed with water and acetone and dried. A tungsten carbide drill was used to obtain the drillings from five points of each coin object. The drillings were combined and used as sample to be analyzed.

Standards and reagents. Ammonium hexachloroosmate and ammonium hexachlororuthenate of specpure grade (obtained from Johnson Matthey Co. Ltd.) were employed as the standards of osmium and ruthenium. The synthetic mixtures were made appropriately by mixing individual standards. Perchloric acid and hydrogen peroxide (3%) were of analytical reagent grade.

Neutron irradiation. About 100 mg of each coin sample, together with ca. 10 mg of standards of osmium and ruthenium were accurately weighed and sealed in the silica glass vials. The synthetic mixtures were treated similarly. A known amount of cobalt as a flux monitor was attached to the surface of each silica vial. The coin samples and the synthetic mixtures were placed together with the standards of osmium and ruthenium in an aluminum capsule and irradiated for 4-5 days at a neutron flux of approximately 1×10^{13} neutrons $\text{cm}^{-2} \times \text{sec}^{-1}$ in TRIGA MARK III Reactor. In the case of the coin samples, the samples were processed after a cooling period of about one week.

Dissolution of irradiated coin samples. The irradiation vials containing the coin samples were opened and the contents were transferred into the teflon cup of an assembly of high strength acid digestion bomb (Parr Model 4748) by gentle tapping. A 10 mL volume of concentrated nitric acid was added. The cup was covered and put into the assembly, which was heated at 150-170°C for 3 hours.

The dissolved solution was transferred to a 200 mL distillation flask. During this manipulation, the cup and the flask were cooled in the ice bath to avoid any loss of osmium and ruthenium. The cup was washed with a minimum amount of nitric acid. The washings of the cup were added to the flask. After this treatment, the activity remaining in the cup was found to be negligible.

Distillation of osmium and ruthenium. The apparatus employed in this work is the same as used by Chung and Beamish.⁵ A 100 mL volume of 72% perchloric acid was added dropwise into a 200 mL distillation flask, during this operation both osmium and ruthenium were simultaneously distilled. The distillate was collected in two receivers containing 3% solution of hydrogen peroxide.⁶ After distillation, the solution in the two receivers was combined into a 200 mL flask (Corning No. 5900) and stored in a refrigerator.

Preparation of standards. The irradiated standards of osmium and ruthenium compounds, $(\text{NH}_4)_2\text{OsCl}_6$ and $(\text{NH}_4)_2\text{RuCl}_6$, were each dissolved with distilled water and diluted to 100 mL. The synthetic mixtures were dissolved similarly. A 1 mL volume of each solution was taken into 200 mL flask and diluted appropriately so as to make the same counting geometry as the above sample solution. The solution was stored as described above. The appropriate aliquot of the above 100 mL solution was also used as the tracer solution of both metals.

Gamma-ray spectrometry and preprocessing of raw data. The activities of the sample and the standards were measured for 1800 sec. by a HPGe solid state detector (EG & G ORTEC Model GEM 150180) which was connected to a 8192 channels analyzer (EG & G MCA system) as well as to a ADC data processing system. Background was also measured after shielding the detector.

From each spectrum in 8192 channels a segment of the spectrum consisting 1800 channels was extracted. The spectrum in 1800 channels, covering the interested gamma energies, was compressed to 900 channels prior to factor analysis.

The programs for AFA as well as for TTEA, written in the Basic language in our laboratory which was based on the equations of Malinowski and Howery,¹ were used for all factor analysis routines. The programs were executed on an IBM-PC compatible microcomputer.

Theory

TTFA belongs to a branch of data analysis techniques known as multivariate techniques. The basis of this technique is that each datum is composed of a linear combination of contributions from the factors. In NAA, the factors are radioisotopes, the objects are samples. The gamma-ray spectra obtained from a set of samples are represented by a data matrix in which columns correspond to samples and rows to channels. Each element of the matrix contains the number of counts recorded in a channel and may be referred to as a datum.

AFA decomposes the data matrix into abstract factors. To accomplish this task, the matrix is multiplied by its transpose to give a covariance matrix which is then subjected to eigenvector/eigenvalue analysis. Each eigenvector gives a direction in data space that accounts for some portion of the variation among the data. Essentially 100% of the variance in any

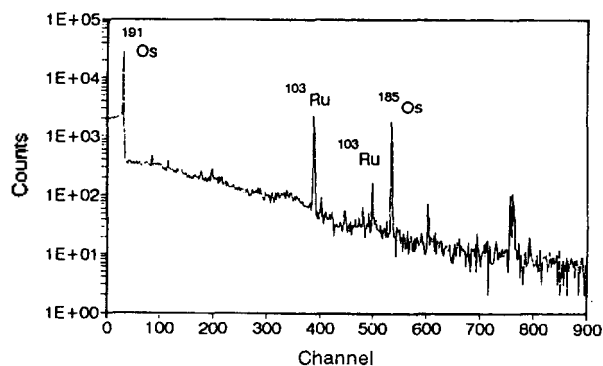


Figure 1. Gamma-ray spectrum of the osmium and ruthenium mixture obtained by distillation. 1800 sec. data accumulation with HPGe solid state detector 1 day after the end of 5 days irradiation of the standard compound of osmium and ruthenium.

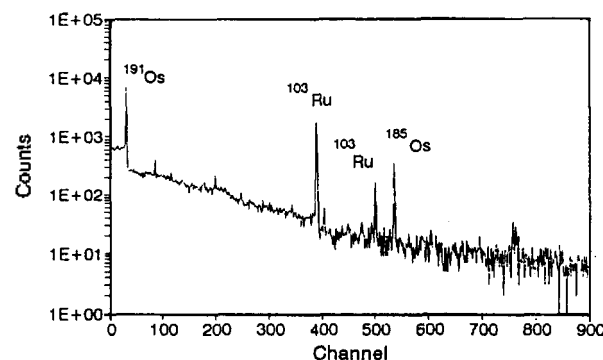


Figure 2. Gamma-ray spectrum of the distillate from the irradiated coins. Irradiation and gamma-ray counting conditions are similar to those of the synthetic mixtures.

data set is contained in the first few eigenvectors. The method of determining the number of significant eigenvectors makes use of eigenvalues. There are numerous methods for determining the cutoff between the significant eigenvectors and the residual eigenvectors.^{1,7,8} The residual eigenvectors are rejected, resulting in reduction in dimensionality and an accompanying reduction in random noise. The remaining eigenvectors, also referred to as abstract factors, span the same space spanned by real factors (radioisotopes present in the sample solution) but do not correspond to them. The transformation to real factor space can be carried out by TTFA. In TTFA, a set of test vectors are individually tested for their presence in the data matrix. The successful test vectors constitute a training set that defines a transformation to radioisotope space. The abstract matrix is transformed by means of the transformation matrix with the result that the columns and rows of the transformed matrix correspond to specified isotope spectra and contribution (loadings) to the spectra. The loadings of the samples give the elemental concentration in the samples if the standard samples are included in the data set.

Results and Discussion

The above distillation procedure and gamma-ray spectrometry were applied to the synthetic mixtures as well as the

Table 1. Recovery of Osmium and Ruthenium by Distillation

Samples	Oxidant	Metal added (μg)	Metal recovered (μg)	Recovery (%)	Receiving solution
$(\text{NH}_4)_2\text{OsCl}_6$	72% HClO_4	34.6	34.6	99.9	3% H_2O_2
$(\text{NH}_4)_2\text{RuCl}_6$	72% HClO_4	23.1	23.0	99.4	3% H_2O_2

After the distillation of the standard compound of osmium and ruthenium, the recovery ratios were determined radiochemically by measuring the photopeak area of 130 keV ^{187}Os and 498 keV ^{106}Ru , respectively. Distillation conditions: Temp. = 150°C, Time = 30 min.

coin samples. The results of the synthetic mixtures, as indicated in Figure 1, showed the gamma peaks of ^{187}Os and ^{189}Os and also ^{106}Ru . A typical spectrum obtained from the coin samples are given in Figure 2 which verifies the simultaneous distillation of these two metals and absence of impurity radioisotope contaminating the gamma-ray spectrum. Table 1 shows quantitative recoveries of both metals during the whole procedure. After the distillation of the standard compound of osmium and ruthenium, the recovery ratios were determined radiochemically by measuring the photopeak area of 130 keV ^{187}Os and 498 keV ^{106}Ru , respectively. The data matrix was made from the pure gamma-ray spectra of each osmium and ruthenium, four coin sample spectra and three synthetic Os/Ru mixture spectra. This matrix (900 \times 9) was subjected to AFA.

The theory of errors was applied to determine the number of factors. The eigenvalues obtained are given in Table 2. Following this, the evaluation of real error (RE), imbedded error (IE), and extracted error (XE) was carried out for all possible numbers of factors. Additionally, successive eigenvalue ratios (λ_n/λ_{n+1}), standard errors in the eigenvalues and indicator (IND) function were evaluated and the AFA results are given in Table 2.

The RE depends upon an accurate estimate of the experimental error, however, such information is not available in this work. Consequently, the IE and IND were used. The IE value should level off and IND value should show a minimum at the correct number of factors, respectively.

Table 3. Target Test of Osmium and Ruthenium on the Data Matrix

Elements	AET	REP	RET	SPOIL
Os	24.0	16.5	17.5	1.07
Ru	19.6	12.1	15.4	1.27

AET = the root mean square of the apparent error in the test vector, RET = the root mean square of the real error in the test vector, REP = the root mean square of the real error in the predicted vector.

The presence of two factors is indicated by the imbedded error, since these values do not decrease significantly beyond the factor number of two. Additionally, the IND values reach a minimum at three factors which means one more than the proper number of factor as noted elsewhere.⁹ The standard errors in the eigenvalues given in the Table 2 reflect the presence of two factors because the eigenvalues and the standard errors in eigenvalues become of comparable magnitude at the factor number of more than two.

After the evaluation of the number of factors present, target tests were individually carried out for the suspected factors. The isotope spectra of standards were used as the test vectors and the decision was made if the spectra were identified as the true spectra in the matrix. For this purpose, the AET (the root mean square of the apparent error in the test vector), RET (the root mean square of the real error in the test vector), REP (the root mean square of the real error in the predicted vector), and SPOIL values¹ have been calculated and are listed in Table 3. The value of SPOIL is especially useful. According to Malinowski, a SPOIL between 0 and 3 is indicative of a real factor and is acceptable; a SPOIL between 3 and 6 is moderately acceptable; a SPOIL greater than 6 is not acceptable. As shown in Table 3, osmium and ruthenium are satisfactorily tested as two factors, i.e., the dimensionality of the data matrix is the same as the number of pure elemental gamma-ray spectra.

Once target testing was completed, a combination step was carried out using successful test vectors and a column matrix containing the concentration of each element in units relative to the standard is obtained. The analytical results of synthe-

Table 2. Factor Analysis of Os and Ru in the Gamma-Ray Energy Range 100-1000 keV

N	Eigenvalue (λ_n)	Ratio (λ_n/λ_{n+1})	Standard error in eigenvalue	RE	XE	IE	IND
1	5.52E+09	58.28	1.45E+07	83.11	78.36	27.70	1.298
2	9.47E+07	25.34	4.71E+06	19.52	17.21	9.203	0.398
3	3.74E+06	6.241	3.73E+06	9.942	8.118	5.740	0.276
4	5.98E+05	3.917	3.76E+06	7.220	5.382	4.813	0.288
5	1.53E+05	1.327	7.91E+06	6.630	4.420	4.941	0.414
6	1.15E+05	1.592	3.05E+06	6.107	3.526	4.986	0.678
7	7.22E+04	1.041	2.23E+06	5.989	2.823	5.282	1.497
8	6.94E+04	1.162	2.25E+06	5.760	1.920	5.431	5.760
9	5.97E+04		1.84E+06				

The data matrix (900 \times 9) was made from the gamma-ray spectra of the two standards, the three mixtures, and the four distillates from the coin samples. N = number of factors; RE = real errors; XE = extracted errors; IE = imbedded errors; IND = indicator functions.

Table 4. Comparisons of the Analytical Results for the Synthetic Mixtures

Samples	Concentration (μg)					
	Composition of sample		Calculated by TTFA		Calculated by single peak	
	Os	Ru	Os	Ru	Os	Ru
1	8.67	5.78	8.42	5.62	8.31	5.50
2	4.34	5.78	4.31	5.98	4.29	5.99
3	4.34	8.67	4.37	8.70	4.22	8.79

All the data were calculated by measuring the gamma-ray spectra of the distillates that were obtained from the irradiated Os and Ru mixtures.

Table 5. Concentrations (ppm) of Os, Ru in the Coin Samples

Samples	Concentration (by TTFA)		Concentration (by Single Peak)	
	Os	Ru	Os	Ru
1	3.75	10.3	3.76	9.07
2	8.49	13.2	8.58	12.7
3	17.6	10.2	17.7	10.3
4	6.55	13.4	6.48	13.1

tic mixtures are given in Table 4. For the comparison of the precision of the two methods in determining the concentrations of both metals, i.e., TTFA and conventional single peak methods, the results obtained by these two methods are included in Table 4. The standard deviation are not shown in Table 4 as we were unable to obtain sufficient data due to the unavoidable situation in our laboratory and the reactor conditions, however, the results obtained by TTFA show that they are a little more precise as compared to those obtained by the single peak method. The analytical results of the coin samples are given in Table 5, in which, the results by conventional method were also given for comparison. In this Table, the results obtained by TTFA were nearly the same as those obtained using the single peak method. However, Table 4 indicates that better precision may be obtainable from the TTFA method.

Various detection limits, i.e., critical, detection, and quantitative limits (10% uncertainty), were calculated by means of the Currie's definitions¹⁰ based on the well-known blank.

$$\text{critical limit} = 1.64 \times B^{1/2}$$

Table 6. Comparisons of Three Limiting Levels (microgram) Calculated by the Single Peak Method and the TTFA Method

	Single Peak Method		TTFA Method	
	Os	Ru	Os	Ru
Lc	0.0119	0.0150	0.00156	0.00165
Ld	0.0238	0.0304	0.00313	0.00332
Lq	0.0735	0.1011	0.00998	0.01059

*Lc: Critical limit, Ld: Detection limit, Lq: Quantitative limit.

$$\text{detection limit} = 2.71 + 3.29 B^{1/2}$$

$$\text{quantitative limit} = k^2/2 \times [1 + (1 + 4B/k^2)^{1/2}]$$

where k is the value of 100 divided by allowable uncertainty in % and B is the total counts of background. The main sources of the background are natural radiation, the Compton scattering and electronic noise. Among them the Compton scattering has a major effect upon the background. In the conventional method, the background is greatly increased by the Compton scattering of the high gamma-ray peaks. However in the TTFA method, because the counts due to the Compton scattering is regarded as the signal, the signal to noise ratio has improved. The results in Table 6 shows that the limits in TTFA are lower by one order of magnitude than the single peaks are used.

Acknowledgement. The present study was supported by the Basic Science Research Institute Program, Ministry of Education, 1991 (BSRI-91-339).

References

1. E. R. Malinowski and D. G. Howery, "Factor Analysis in Chemistry", Wiley, New York, 1980.
2. I. A. Crowe and J. W. McNicol, *Appl. Spectrosc.*, **39**, 257 (1985).
3. D. F. Wirsz and M. W. Blades, *Anal. Chem.*, **58**, 51 (1986).
4. D. D. Burgess, *J. Radioanal. and Nucl. Chem.*, **123**, 377 (1988).
5. K. S. Chung and F. E. Beamish, *Talanta*, **15**, 823 (1968).
6. A. D. Westland and F. E. Beamish, *Analyt. Chem.*, **26**, 739 (1954).
7. E. R. Malinowski, *Anal. Chem.*, **49**, 606 (1977).
8. E. R. Malinowski, *ibid.*, 612 (1977).
9. M. McCue and E. R. Malinowski, *Appl. Spectroscopy*, **37**, 463 (1983).
10. L. A. Currie, *Anal. Chem.*, **40**, 586 (1968).