

The Analysis of Small Glass Fragments Using Inductively Coupled Plasma Mass Spectrometry

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ABSTRACT: Inductively coupled plasma mass spectrometry using solution nebulization has the ability to analyze up to 70 elements with good precision, accuracy, and sensitivity and is, therefore, well suited for the trace element analysis of glass. However, the technique places severe restrictions on sample preparation. High concentrations of acids or dissolved solids, changes in sample viscosity and molecular compound formation can cause physical, spectral and chemical interference. Solubilization of the glass samples based on a three acid digestion procedure (HF, HNO₃, HCl 2:1:1) has been found to minimize these problems. Up to 62 elements have been determined in a range of glass samples. Glasses that could not be distinguished on the basis of refractive index measurement could be discriminated. A procedure of measuring a range of elemental ratios, which eliminated the need for weighing, was used to compare small samples typical of casework.

KEYWORDS: forensic science, criminalistics, mass spectrometry, inductively coupled plasma mass spectrometry, glass, trace evidence

Refractive index (RI) measurement is the basic method used for the comparison of small glass fragments in most forensic science laboratories. Elemental analysis can provide valuable additional information, particularly where RI has failed to discriminate two glasses. Variation in major element concentrations will tend to be associated with a change in refractive index, while trace element (TE) variations may not be revealed in the optical properties of the glass. It is important therefore that any technique used for the elemental analysis of glass be capable of detecting a wide range of elements at trace levels (ng/g to low µg/g) in order to discriminate glasses that have similar refractive indexes.

A range of spectroscopic techniques have been used for the trace element analysis of glass, including atomic absorption (1), spark source mass spectrometry (2), neutron activation (1), emission spectrography (3) and X-ray fluorescence (4). Inductively coupled plasma atomic emission spectrometry (ICPAES) combines a multiple element capability with good sensitivity and has been the most extensively used technique in recent times (1,4-9).

Inductively coupled plasma mass spectrometry (ICPMS) using

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solution nebulization is capable of rapidly determining up to 70 elements with high sensitivity (µg/L level) with precision and accuracy. Zurhaar and Mullings (10) have shown that ICPMS is capable of determining 48 elements in glass fragments weighing as little as 500 µg. They found that 15 elements used as the primary discriminating group allowed glasses of identical refractive index to be differentiated.

An important step in the analysis of glass by ICP techniques is the digestion procedure to produce a suitable working solution. The use of hydrofluoric, hydrochloric and perchloric acids have been reported for this purpose (4,10). The chlorinated acids can produce interfering molecular chloride species and volatile chlorides, which can be lost. A quartz sample introduction system for aspiration of the analytical solution offers high sensitivity, precision and accuracy (11). However, such a system has low HF tolerance and requires that dissolved solids should be lower than 0.5% and preferably less than 0.1%, placing further restrictions on the digestion procedure.

The purpose of this work was firstly to find a suitable digestion procedure for glass that minimized interferences, loss of elements in the form of volatile salts and permitted use of a quartz sample introduction system. The application of ICPMS to the forensic analysis of glass was then investigated, paying attention to the following issues; the ability to discriminate glasses with matching refractive index, the ability to analyze small fragments (<1 mg) and the minimum volume that could be used for sample nebulization. A method using elemental ratios for the comparison of glasses was developed to enable the analysis of samples too small to weigh accurately.

Materials and Methods

Glass Samples

Thirteen pairs of clear glass samples, comprising sheet glass (building window and vehicle window), container glass and borosilicate glass (headlamp) were selected from the authors' laboratory glass collection. The samples consisted of fragments of glass (between 2 g and 20 g) that had been collected from various glass objects. Each pair was chosen on the basis that the samples under comparison could not be discriminated by refractive index measurement but were known to be from different objects. Samples with RI values that matched to 4 decimal places were considered indistinguishable.

Four further pairs of glasses, also from different objects were selected. These glasses had close, but different, RI values (the RI values matched to only the third decimal place).

The refractive index of each glass sample was determined by

the standard oil immersion method in a GRIM automated refractive index system (Foster & Freeman, UK). This involved crushing the sample and mounting it in precalibrated refractive index oil (Locke Scientific, Basingstoke, Hants., UK), followed by heating on a Mettler microscope hot-stage to obtain the match temperature in monochromatic light at 589.3 nm (the sodium D-line). In most cases ten determinations were made, giving a precision of about $\pm 0.2^\circ\text{C}$ which is equivalent to a refractive index of about ± 0.00008 .

Reference Glasses—Two reference glasses SRM 615 with a nominal trace element concentration of 1 ppm and SRM 613 with a nominal trace element concentration of 50 ppm (National Institute of Standards Technology, Gaithersburg, MD) were used as reference standards.

Trace Element Distribution Studies—Intra sample trace element variations were studied in sheet glass. The study was limited to a windscreen laminate and two window glasses, one of which was an old non-float glass. Three large sheets of clear glass were used to establish the extent and significance of trace element concentration variance: *G*, an approximately 40-year-old window (80 cm \times 60 cm); *H*, a section of a broken float window glass (40 cm \times 30 cm); and *L*, a float vehicle windscreen laminate (approximately 120 cm \times 55 cm). Five samples, each consisting of several pieces that weighed in total about 2 g, were taken from the four corners and near the center of each window glass. These points were selected for maximum distance between samples. Both sheets of the windscreen laminate (outer sheet LO and inner sheet LI) were also sampled at the corners. The fifth sample from each sheet was taken at a point of breaking sustained during a vehicle accident (at the mid-point of the windscreen and about 28 cm from one end). The samples within each set of glasses *G*, *H*, *LO* and *LI* had *RI* values differing by ± 0.00003 , ± 0.00004 , ± 0.00002 and ± 0.00004 respectively and were considered indistinguishable. Furthermore, the glasses *LO* and *LI* were also indistinguishable (*RI* value differed by 0.00008).

Twelve glass samples (including three mirror glasses) that represented three international proficiency testing trials (Collaborative Testing Services, Herndon, VA) provided additional means to evaluate the method.

Sample Preparation

Analysis of small fragments can highlight lack of homogeneity of glass, so each of the laboratory glass collection samples was subsampled for analysis by taking multiple fragments (usually by breaking pieces off the sample fragments) to ensure a representative sample.

Mirror fragments were scraped clean of the backing with a scalpel before sampling. Soiled glass was rinsed with de-ionized water and wiped clean with a facial tissue soaked in methanol.

Samples were finally cleaned by immersion in 50% nitric acid for half an hour. After rinsing with de-ionized water and air drying, the samples were crushed between polyethylene sheets in an acid-washed agate mortar. Fragments weighing less than 2 mg were selected for analysis and were combined to give samples of about 200 mg. The samples were stored in clean Eppendorf polypropylene tubes.

The leaching of analytes during this 50% nitric acid washing procedure was insignificant, as evidenced by the results obtained from the multiple analyses of reference glasses SRM 613 and SRM

615 over a period of six months (Tables 4 and 5). Similar results were obtained for several pairs of glasses, for example, samples 4 and 7 (Fig. 4).

Digestion

A number of digestion procedures were trialed as discussed in the Analytical Methods Development section and the final procedure was as follows:

10 mg of glass was placed in a 5 mL polypropylene tube (15 mm ID \times 40 mm) with a hinged cap. An acid mixture consisting of 300 μL HF (Aristar), 150 μL HNO₃ (Merck AR, double glass distilled), and 150 μL HCl (Aristar) was added and the tube capped. The tube was sonicated until the glass decomposed (about 60 min). The solution was evaporated to dryness at 80°C (Pierce Reacti-Therm heating module) and 1000 μL of 50% HNO₃ and 2000 μL of purified water (Hi-Pure Water Systems, Permutit, Australia) added. The solution was sonicated until clear (<30 min) and transferred to a 15 mL polypropylene tube containing 100 μL of a 10 $\mu\text{g}/\text{mL}$ rhodium solution as internal standard (IS). A final dilution to 10 mL with water was made (equivalent to 5% HNO₃).

For the digestion of smaller glass samples the volume of the acid mixture and the final dilution volume was reduced proportionately maintaining 5% HNO₃. The protocol was followed to maintain uniformity between samples under comparison and to reduce the number of blanks carried through the procedure. Samples weighing less than 1 mg were diluted to the minimum final volume of 2 mL. Each batch of analyzed glass included duplicate blanks and standard reference glasses SRM 613 (10 mg/15 mL) in duplicate or SRM 615 (20 mg/10 mL) in duplicate, together with their respective blanks.

The evaporation step removed silicon and residual acids from the glass digest. The remaining dissolved solids in the final sample solutions did not interfere with the measurement of trace elements and therefore samples and standards were matched by acid content only (5% HNO₃).

Standard Solutions

A reference solution containing 48 elements (Table 1) at 1 $\mu\text{g}/\text{mL}$ in 5% HNO₃ was prepared from 1000 $\mu\text{g}/\text{mL}$ single element Spex plasma standard solutions (Spex Industries Inc., Edison, NJ,

TABLE 1—Elements monitored for discrimination between glass samples.

Elements in Working Standards			Additional Elements
Li	Y	Eu	Be
Mg	Zr	Gd	B
Al	Pd	Tb	Ca
Ti	Ag	Dy	Sc
V	Cd	Ho	Zn
Cr	In	Er	Ga
Mn	Sn	Tm	Nb
Fe	Sb	Yb	Mo
Co	Te	Hf	Lu
Ni	Cs	Re	Ta
Cu	Ba	Au	W
Ge	La	Tl	Os
As	Ce	Pb	Ir
Se	Pr	Bi	Pt
Rb	Nd	Th	
Sr	Sm	U	

USA) via a set of 9 intermediate standard mixes (10 $\mu\text{g/mL}$). The reference solution was further diluted with 5% HNO_3 to produce a set of working standard solutions of 10 to 100 ng/mL , each containing 100 ng/mL rhodium (IS). Rhodium was chosen as the internal standard, being in the middle of the mass range and being rarely encountered in the environment.

All micropipettes were calibrated by mass. All glassware and plasticware, with the exception of the Greiner tubes (see Analytical Methods Development Section) were cleaned by immersion in 10% HNO_3 for 24 h, rinsed with de-ionized water and air dried. Volumetric flasks, and plastic containers used for the prolonged storage of intermediate standard mixes, were further equilibrated with de-ionized water for 24 h after acid-washing.

All acids were diluted by volume. All manipulations were carried out in a dust free environment (class 100 clean room).

Instrumentation

A VG PlasmaQuad™ ICPMS system (VG Isotopes, Winsford, UK) was used. The plasma torch was quartz with a quartz injector, and sample introduction was via an all-quartz Scott spray chamber and Meinhard nebulizer system.

Sample solutions containing glass matrix dissolved in HF/HNO_3 mixtures were processed via a corrosion resistant nebulization kit. The PTFE spray chamber of this kit was subsequently replaced with the Scott variant to enhance count rate, reproducibility and precision.

Instrument Parameters

Gilson Minipuls 3 Peristaltic pump	Setting 48, 1.0 mL sample flow/min for the corrosion resistant configuration Setting 35, 0.7 mL sample flow/min for the all-quartz system
Gases (argon)	Nebulizer 0.8 L/min Auxiliary 0.5 L/min Coolant 14.0 L/min
Generator	Henry 2.5 kW Operating power 1.4 kW

Data Acquisition

Measurement mode	SCAN or PEAK JUMP
No of points/peak (PEAK JUMP mode)	3
Mass range	6 to 240 amu
Channels (DAC steps)	2048
Dwell time/channel	320 μs , SCAN mode 10,000 μs , PEAK JUMP mode
No of sweeps/measurement	100
Measurement/sample	5

Instrument Set-up

Warm up	Minimum 30 min
Tuning	Count rate for ^{103}Rh optimized before data acquisition (90,000 to 120,000 ACPS)
Resolution	Set to give at least two orders between peaks of equal height under stated parameters

Data Acquisition and Processing

Sixty-two (62) elements in the relative atomic mass range from 7 (Li) to 238 (U) were monitored (Table 1). Preliminary scans were performed on each glass sample to determine the elements that could be used for discrimination between glasses. Raw counts were processed using the VG PlasmaQuad™ software to produce integrals that represented the area counts per second (ACPS) for at least one isotope for each element determined. Five measurements were taken for each element in each sample. The ACPS were ratioed to the IS and then corrected for blank counts (also relative to the IS). These corrected relative responses (CRR) were used to calculate an elemental ratio and concentration ratio as follows:

Elemental Ratio—The five CRR for each element in a sample were first each ratioed to the five CRR of another element of similar mass (for example, Ba and La) in the same sample. Each of these element-pair ratios was then ratioed to the five corresponding element-pair ratios in the sample under comparison, resulting in 25 permutations for each element-pair, the mean of which (± 3 standard deviations) was defined as the elemental ratio.

Concentration Ratio—The five CRR for each element in a sample were further corrected for sample weight, and then each was ratioed to each of the five CRR for the same element in the sample under comparison, again resulting in 25 permutations for each element in each analysis. The mean (± 3 standard deviations) derived from these permutations was defined as the concentration ratio.

When samples were analyzed in duplicate or triplicate the number of permutations from which the mean was derived was 100 and 225, respectively.

Analytical Methods Development

Several digestion procedures using sheet glass (window) were trialed in combination with various sample introduction configurations.

HF/HNO₃ Digestion (Without Removal of Si)—10 mg of glass was placed in a 50 mL Greiner tube (Greiner brand, Germany), an acid mixture consisting of 150 μL HF and 500 μL HNO_3 added and the tube capped. The tube was sonicated until the glass decomposed (60 min). The sample was diluted to 5 mL with water and further sonicated until clear (<30 min). 100 μL of 10 $\mu\text{g/mL}$ rhodium (IS) and 1000 μL of 1% m/v Triton X-100 surfactant (LR grade) were added before dilution to 10 mL was made. The final solution contained 5% HNO_3 , 0.1% Triton and an approximate excess of 1% HF. It was estimated that about 50 μL of the total volume of HF was necessary to decompose 10 mg of glass, the remaining volume being excess. Duplicate blanks were included for trials.

Digests adjusted to contain 0.5, 1, 2 and 5% HF in the final solution were prepared to assess the recovery of TE in solution and the corrosive effect of HF on the system. Digests adjusted to contain 0.01, 0.02, 0.05 and 0.1% Triton in the final solution were used to assess PTFE nebulizer efficiency.

Preliminary experiments with sample introduction configurations revealed that:

- The corrosion resistant kit comprising an alumina injector, PTFE V-groove nebulizer and a PTFE spray chamber gave poor

results. Solutions containing 0.1% Triton gave the most reproducible readings for analytes.

- The replacement of the PTFE chamber with the Scott variant doubled the count rate and enhanced reproducibility and precision.

- Blank levels were generally low across the entire mass range irrespective of HF concentration (<0.1 ng/mL). Only B, Cu, Zn and Pb gave elevated counts. The excess fluoride ions entering the plasma did not affect the Ni skimmer cone as they did in the work reported by Zurhaar and Mullings (10), (Fig. 1). SiF_3^+ species obscured a few elements such as ^{85}Rb (Table 5).

- Blank solutions containing 0.1% Triton did not show significant background interferences. However, elevated counts at 52 amu due to ArC^+ interfered with the assessment of Cr.

- Silicon fluoride species were proportional to HF concentration (Fig. 1). The abundance of these species was greater when the Scott spray chamber was used.

- Sample solutions containing 1% HF were visibly free of insoluble fluorides and gave the highest recoveries for many elements (Fig. 2).

Initial analyses of window glasses indicated that samples could be discriminated using two standard deviations, but they could not be discriminated using three standard deviations, because the high levels of Si (about 330 $\mu\text{g}/\text{mL}$) in the sample solutions created severe matrix suppression and drift in elemental response. Quality quantitative data was difficult to obtain and discrimination of glasses on this basis was not possible. Elemental ratios, however,

offered a means of sample comparison unaffected by drift and less affected by suppression.

Dilution of the sample digest was investigated as a way of overcoming the problems caused by the high Si matrix concentration. Standard SRM 613 glass samples digested by this procedure but diluted to 30 mL (dilution 1:3000) and adjusted to contain 1% HF, 5% HNO_3 and 0.1% Triton, gave acceptable quantitative data (Table 2). The comparison of elemental ratios also indicated that dilute glass matrix (1:3000) can be used for the discrimination of glass samples containing TE in the $\mu\text{g}/\text{g}$ range (Table 3). However, such a large dilution factor would create detection problems for TE in the ng/g range.

Removal of Si Matrix—The need to modify the glass matrix without diluting analyte species was resolved by removal of Si by evaporating the digested samples to dryness. As the boiling points of SiF_4 , HF and SiCl_4 are -86°C , 19.7°C and 57.6°C respectively, heating to 80°C and 90°C was tested to assess the loss of silicon. A variety of acid mixtures for the digestion and subsequent dissolution of digested glass samples was further investigated to assess

TABLE 2—Replicate ICPMS results for NBS standard glass SRM 613. Glass matrix dilution 1:3000 in 1% HF, 5% HNO_3 .

Element	CERT $\mu\text{g}/\text{g}$	SRM 613 Scan Mode				RSD %
		ICPMS Sample a $\mu\text{g}/\text{g}$	ICPMS Sample b $\mu\text{g}/\text{g}$	ICPMS Sample c $\mu\text{g}/\text{g}$	ICPMS (mean) $\mu\text{g}/\text{g}$	
Mn	(39.6 ± 0.8)	39	41	36	38	7.0
Co	(35.5 ± 1.2)	36	36	33	35	6.0
Ni	(38.8 ± 0.2)	40	43	39	41	4.2
Cu	(37.7 ± 0.9)	36	40	34	37	8.2
Rb	31.4 ± 0.4	30	31	29	30	3.5
Sr	78.4 ± 0.2	72	80	76	76	5.3
Ag	22.0 ± 0.3	24	25	21	23	8.0
Ba	(41)	35	41	39	38	7.3
Nd	(36)	37	36	36	36	1.4
Sm	(39)	37	44	39	40	8.8
Pb	38.6 ± 0.2	37	42	41	40	6.1
Th	37.8 ± 0.08	36	40	38	38	5.6
U	37.4 ± 0.08	35	40	38	38	6.4

NOTE:—NBS—US National Bureau of Standards, SRM—standard reference material, CERT—values as per NBS Certificate, values in parentheses are interim, and RSD—relative standard deviation.

TABLE 3—Replicate values of Elemental Ratios for NBS standard glass SRM 613. Glass matrix dilution 1:3000 in 1% HF, 5% HNO_3 .

Elemental Ratios	SRM 613 Scan Mode				% RSD
	Sample a	Sample b	Sample c	Sample d	
Mn/Co	1.08	1.12	1.09	1.11	1.7
Co/Ni	0.88	0.85	0.83	0.91	4.0
Ni/Cu	1.12	1.07	1.16	1.11	3.2
Cu/Rb	1.21	1.27	1.16	1.17	4.3
Rb/Sr	0.42	0.39	0.39	0.40	3.1
Sr/Ag	2.96	3.21	3.54	3.64	9.3
Ag/Ba	0.68	0.61	0.55	0.57	9.6
Ba/Nd	0.97	1.15	1.08	1.12	7.4
Nd/Sm	0.99	0.82	0.92	0.96	8.3
Sm/Pb	0.99	1.04	0.96	1.06	4.5
Pb/Th	1.04	1.05	1.07	0.97	3.9
Th/U	1.02	1.00	1.00	1.02	1.0

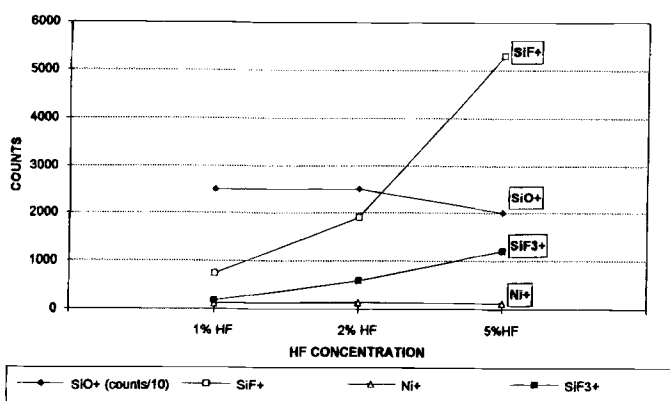


FIG. 1—Relationship between HF concentration and silicon molecular species. Monitoring of Ni cone degradation.

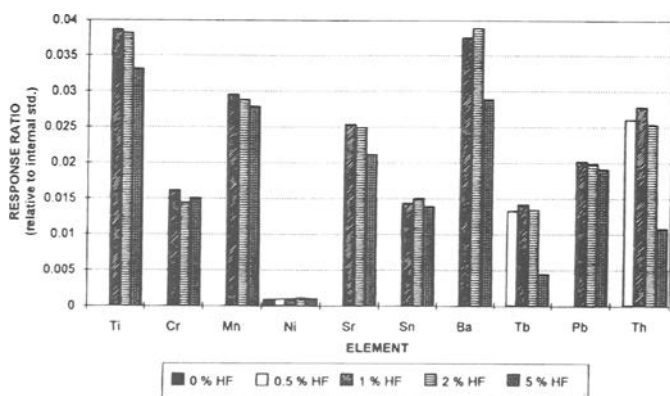


FIG. 2—Effect of HF concentration on elemental recovery.

(i) maximum recovery of elements that form insoluble fluorides or volatile fluorides and chlorides, and (ii) minimum molecular interferences in the final solution for measurement. The protocol used was similar to that in the section on Digestion.

A single pair of door glasses (4 and 7) with identical refractive index values and very similar TE profiles was chosen for the investigations. A triplicate set of samples from each glass, together with samples of glass standard SRM 613 and matching blanks, was used to assess the viability of each procedure. Particular attention was given to the recoveries of Ge, Se, As and Sb as they are good examples of elements that form volatile fluorides and chlorides. All sample solutions with modified glass matrix (that is, with Si removed) were analyzed via the all-quartz sample introduction system. The nebulizer spray chamber was washed with 10% HNO₃ for 90 s between samples, followed by 30 s wash time with the next sample. A further 30 s were allowed for the system to stabilize.

The following conclusions were made:

- The HF/HNO₃ (1:1) acid mixture for digesting glass produced the highest amount of insoluble fluorides. The HF/HNO₃ glass digests evaporated to dryness at 80°C and 90°C respectively and then dissolved to contain 5% HNO₃ in the final solution, were clear. Trace element ratios obtained for the respective test solutions were similar, suggesting no apparent loss of TE due to heating in the temperature range of 80°C to 90°C. The evaporation step effectively removed residual acids and most of the silicon (Fig. 3). Glass digests dissolved to contain 2% HNO₃, 2% HCl showed a marked decrease in the absolute counts for many elements.

- The HF/HCl (1:1) combination was most effective for the dissolution of insoluble fluorides and the digests were almost clear. Samples evaporated at 80°C and then dissolved to contain 2% HCl in the final solution gave the lowest counts for most elements resulting in reduced sensitivity and precision. These solutions also gave the highest counts for Si, suggesting less efficient removal of this element at the digestion step (Fig. 3).

- The HF/HNO₃/HCl (2:1:1) digestion enhanced the dissolution of insoluble fluorides. Glass digests evaporated at 80°C and dissolved to contain 2% HNO₃, 2% HCl generated chloride ions that interfered with the determination of several elements including As and the ⁷⁷Se isotope. The counts for As and ⁷⁷Se were elevated due to argon chloride. The remaining Se isotopes suffered interference from the argon dimer and krypton (traces in the Ar) and therefore the recovery of Se could not be assessed accurately.

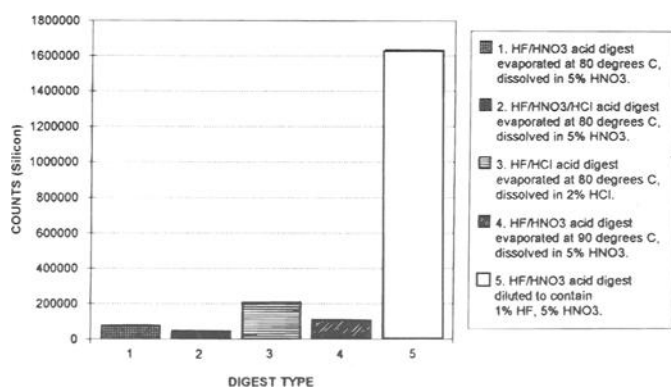


FIG. 3—Residual silicon content of glass sample solutions obtained by various digestion procedures. Results for glass 4.

Glass digests evaporated at 80°C and dissolved to contain 5% HNO₃ in the final solution had the lowest amount of Si and interfering chloride species, and produced the best results for the majority of elements determined which compared favorably with certified values (Table 4). The blank values for the majority of elements were less than 50 ACPS. Elevated counts (<1000) were registered for V, Cr, Cu, Zn, Ba and Pb and only Al and Fe gave counts in excess of 1000. Preliminary studies using glass standard SRM 613 spiked with Ge, Se, As and Sb at 50 µg/g respectively showed recoveries of 75% (Se), 85% (Ge, As) and 95% (Sb). For these reasons the procedure described in the section on Digestion was adopted for this study.

The method of Zurhaar and Mullings (10) was not pursued. It was based on the dissolution of glass in a mixture of HF/HCl/HClO₄, which required specialized and expensive PTFE digestion vessels and a custom-made heating block of high-density aluminum. The presence of HClO₄ and HCl in the final solutions was not desirable. Furthermore, the results of the analyses of glass samples and standards by the final procedure (see section on Digestion) have shown that the total removal of fluorides from the analyzed solutions was not required but for a few exceptions such as ⁸⁵Rb.

- The analyses of glasses 4 and 7 revealed that the elemental ratios were constant and reproducible with time irrespective of the digestion procedure used. The glasses were discriminated by the Sr/Ba ratio and the results were reproduced by seven independent determinations of replicate samples using three different digestion procedures over a period of 6 months (Fig. 4).

Results and Discussion

Accuracy, Precision, and Sensitivity

These were assessed using the NBS standards and the results are shown in Tables 4 and 5. Overall the ICPMS results gave excellent agreement with the certified data. These results also indicate that almost 100% recovery of the elements was achieved using the adopted digestion procedure. Interference from CaO⁺ in the case of Co and Ni and from SiF₃⁺ in the case of Rb caused some variation from the certified data for these elements (Table 5).

The drift in elemental response was about 10% over a typical analysis period of 6.5 h (Fig. 5). Contributory factors to this

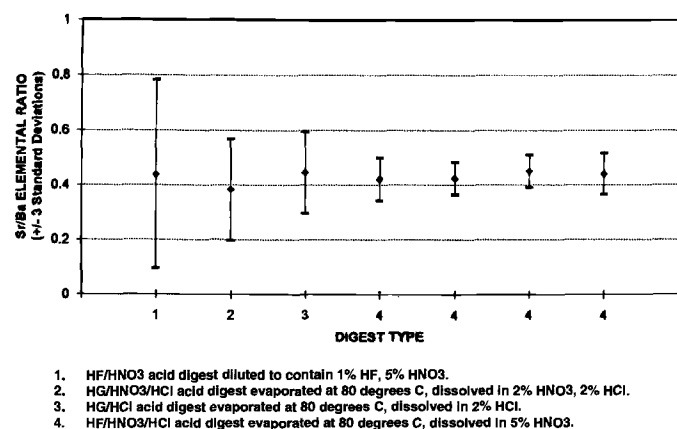


FIG. 4—Comparison of samples 4 and 7 based on the elemental ratios Sr/Ba. Results of seven independent determinations over a period of six months.

TABLE 4—Summary of results for NBS glass standard SRM 613. All concentrations are in $\mu\text{g/g}$.

Element	NBS Certificate Values	ICPMS Results	RSD, %	Element	NBS Certificate Values	ICPMS Results	RSD, %
Li		37.2 ± 1.8	6.6	Ba	(41)	39.5 ± 1.7	6.1
Ti	(50.1 \pm 0.8)	45.9 ± 2.3	6.4	La	(36)	35.6 ± 1.1	4.4
V		31.4 ± 2.2	9.8	Ce	(39)	37.7 ± 0.8	3.0
Cr		37.0 ± 0.7	2.5	Pr		38.4 ± 0.9	3.3
Mn	(39.6 \pm 0.8)	38.8 ± 0.6	2.0	Nd	(36)	35.7 ± 0.8	2.9
Co	(35.5 \pm 1.2)	35.6 ± 1.0	3.8	Sm	(39)	36.7 ± 1.5	5.5
Ni	(38.8 \pm 0.2)	39.0 ± 1.0	3.7	Eu	(36)	35.4 ± 1.1	4.4
Cu	(37.7 \pm 0.9)	36.6 ± 1.7	6.4	Gd	(39)	37.3 ± 0.5	2.0
Ge		37.8 ± 0.8	2.4	Tb		36.9 ± 0.7	2.5
As		34.6 ± 1.2	4.8	Dy	(35)	34.6 ± 0.7	3.0
Se		19.0 ± 2.2	16	Ho		38.0 ± 1.0	3.5
Rb	31.4 ± 0.4	32.1 ± 0.5	2.0	Er	(39)	37.8 ± 1.2	4.4
Sr	78.4 ± 0.2	77.9 ± 1.0	1.8	Tm		37.3 ± 0.9	3.5
Y		36.2 ± 0.7	2.8	Yb	(42)	38.0 ± 1.1	4.1
Zr		36.3 ± 0.8	2.5	Hf		36.4 ± 2.8	9.1
Pd		1.47 ± 0.09	8.1	Re		6.46 ± 0.15	3.3
Ag	22.0 ± 0.3	22.3 ± 0.7	4.0	Au	(5)	5.91 ± 0.16	3.3
Cd		28.8 ± 0.9	4.4	Tl	(15.7 \pm 0.3)	15.2 ± 0.4	4.0
In		37.5 ± 1.0	3.8	Pb	38.57 ± 0.2	37.6 ± 1.1	4.1
Sn		39.5 ± 0.6	2.2	Bi		32.8 ± 1.1	4.7
Sb		35.9 ± 0.9	3.4	Th	37.79 ± 0.08	37.2 ± 1.2	4.4
Cs		40.8 ± 1.1	3.9	U	37.38 ± 0.08	37.1 ± 1.2	4.4

NOTE:—i. The results for SRM 613 represent the mean from ten determinations over a period of six months. All measurements were made in the scan mode.

ii. Values in parentheses are interim.

iii. The ICPMS results are presented as the mean \pm the confidence interval, calculated using the expression:

$$\text{Mean } \pm \frac{\text{Student } t \text{ variable} \times \text{standard deviation}}{\sqrt{\text{number of determinations}}}$$

TABLE 5—Summary of results for NBS glass standard SRM 615. All concentrations are in $\mu\text{g/g}$.

Element	NBS Certificate Values	ICPMS Results	RSD, %
Mn		1.49 ± 0.08	6.5
Co	(0.73 \pm 0.02)	$1.9 \text{ (CaO}^+)$	12
Ni	(0.95)	$2.3 \text{ (CaO}^+)$	20
Cu	1.37 ± 0.07	1.54 ± 0.16	12
Rb	0.855 ± 0.005	$3.4 \text{ (SiF}_3^+)$	
Sr	45.8 ± 0.1	48 ± 2	4.1
Ag	0.42 ± 0.04	0.41 ± 0.01	4.3
Ba		3.3 ± 0.2	7.8
La	(0.83 \pm 0.02)	0.74 ± 0.04	7.0
Ce		0.78 ± 0.03	3.9
Nd		0.74 ± 0.04	5.8
Sm		0.76 ± 0.04	6.6
Au	(0.5)	0.47 ± 0.04	9.0
Tl	(0.269 \pm 0.005)	0.27 ± 0.01	6.5
Pb	2.32 ± 0.04	2.36 ± 0.20	9.9
Th	0.748 ± 0.006	0.74 ± 0.06	10
U	0.823 ± 0.002	0.80 ± 0.04	6.7

NOTE:—i. The results for SRM 615 represent the mean from eight determinations over a period of six months. Measurements were made in either the scan or peak jump mode.

ii. Values in parentheses are interim.

iii. Molecular species in parentheses indicate interference.

iv. The ICPMS results are presented as the mean \pm the confidence interval, calculated using the expression:

$$\text{Mean } \pm \frac{\text{Student } t \text{ variable} \times \text{standard deviation}}{\sqrt{\text{number of determinations}}}$$

stability were the efficient removal of silicon (>90%) and the removal of residual HF and HCl by the digestion procedure. Further minimization of interfering molecular species was achieved by maintaining the working solutions in 5% HNO₃.

The detection limits and the precision of the analysis were dependent on the concentration, ionization characteristics and the abundance of the measured isotopes of the determined elements. Relative standard deviations (RSD) of less than 5% were achieved for most elements (Table 4).

The best counting statistics were achieved when 5 mL of a 1 mg/mL glass digest was aspirated. This measured trace elements in the ng/mL range in solution, which is equivalent to $\mu\text{g/g}$ level in glass. Many trace elements of interest are in this range. The achievable detection limits for most elements were from 0.1 to 0.5 ng/mL in solution (equivalent to the lowest meaningful detection

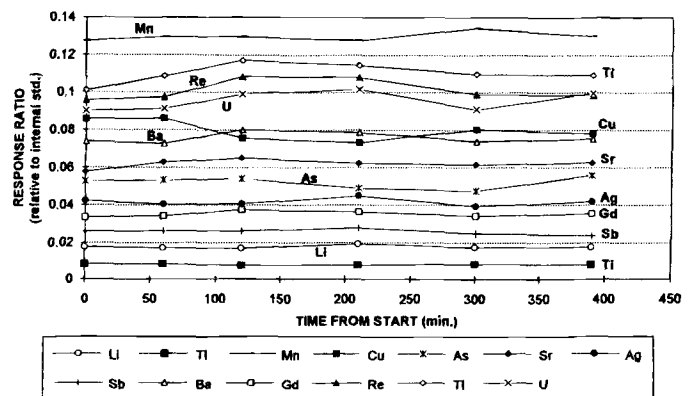


FIG. 5—Drift in elemental response (final digestion procedure).

response range of 100 to 500 ACPS for the measured isotopes). Our experimental data have shown that the smallest glass fragments from which meaningful results could be obtained were of the order of 200 µg. The minimum sample volume that could be used for aspiration was 2 mL.

Discrimination of Glasses

The concentration ratios and elemental ratios as described in the section on Data Acquisition and Processing provide a useful tool for the comparison of glass samples. Both ratios can be determined without knowing absolute concentrations, and elemental ratios are also independent of mass. Most ratios used for the discrimination of glasses were obtained from triplicate analyses.

Glasses were considered *indistinguishable* when all ratios (including three standard deviations) encompassed unity. Conversely, two glasses could strictly be considered *different* when their ratios (including three standard deviations) differed from unity for at least one element. However, inspection of the glass comparison results in the study showed that in all cases of glasses that were different, the ratios for at least one element differed from unity by 20% or more. Thus, a minimum difference of 20% in the ratios (including three standard deviations) for at least one element was adopted as a practical criterion of *difference*. This conservative approach is appropriate for forensic work in that it has the effect of limiting the possibility of Type II errors, that is, incorrectly ascribing two samples to a common source, and is similar to that adopted by Koons et al. (4).

Using this criterion, each of the glasses *within* the 17 pairs studied could be discriminated on at least one element and the results are shown in Table 6, together with the elements that provided discrimination.

TABLE 6—Elements determining discrimination between glass samples.

Samples Compared	Refractive Index	Glass	Discriminating Elements
1 and 2	1.51902/1.51906	W	Al,V,Cr,Mn,Fe,Co,Cu,Rb,Y,Zr, Ba,RE,Hf,Pb,Th
3 and 9	1.51867/1.51896	W	Mn,Zr
4 and 7	1.51908/1.51907	D	Ba(Sr/Ba ratio)
5 and 10	1.51597/1.51591	W	Rb,Sr,Nb,Ba,RE
6 and 8	1.51988/1.51974	W	Al,V,Y,Zr,Ba,RE,Pb
11 and 20	1.51851/1.51850	VW	Zn,Ba
12 and 14	1.51834/1.51832	VW	Zn
13 and 19	1.51835/1.51829	VW	V,Cr,Mn,Co,Ni,Rb,Sr,Y,Zr,Ba, RE,Hf,Ta,Pb,Th,U
15 and 16	1.51625/1.51641	VW	V,Zn,In
17 and 18	1.51823/1.51837	VW	Zr,Pb
21 and 22	1.51592/1.51587	VH	V,Mn,Cu,Zn,Ga,As,Rb,Sr,Zr,Nb, Mo,Sb,Cs,Ba,Hf,Th
23 and 27	1.51537/1.51540	VH	Li,Be,Cr,Mn,Fe,Zn,Ga,As,Rb,Sr, Y,Zr,Nb,Mo,Ag,Cd,Sb,Cs,Ba, RE,Hf,Ta,W,Pb,Th,U
24 and 25	1.51770/1.51773	VH	V,Cr,Mn,Ni,Ga,Rb,Sr,Nb,Mo,Sb, Ba,RE,Pb,Th
26 and 28	1.51564/1.51571	VH	Zn,Zr,Sb,Pb
30 and 31	1.51775/1.51784	C	Mn,As,Ag,Sb,Ba,Pb
29 and 32	1.52180/1.52180	C	Li,As,Rb,Sr,Y,Zr,Nb,RE,Hf,Ta, Th,U
33 and 34	1.51955/1.51956	C	Li,Cr,Mn,Fe,Co,Zn,As,Rb,Sr,Y,Zr, Mo,Cd,In,Sb,Ba,RE,Hf,W,Pb,Th

NOTE:—W—window glass, D—door glass, VW—vehicle window glass, VH—vehicle headlamp glass, C—container glass, and RE—rare earth elements.

glass differed over a wide range of elements and were very easily discriminated. The building window and vehicle window glasses had low concentrations of trace elements and were more difficult to discriminate. Three pairs of these glasses (3 and 9, 11 and 20, 12 and 14) differed in only a few ratios but they could still be clearly discriminated. For example, the discrimination of samples 11 and 20 was based on two elements (Zn and Ba—Fig. 6). The most difficult pair of glasses to discriminate was 4 and 7 (door glass). They could not be discriminated by RI even though 4 was a float glass and 7 was a laminated float glass. However, they were discriminated by the present ICPMS technique, but only on the Ba concentration ratio (Fig. 7).

It can be seen from Table 6 that the elements that provided discriminatory information varied widely between the different sample pairs. The most common elements used, however, were Mn, Zn, Rb, Sr, Zr, Ba, Pb, Th, and the rare earth elements. Caution should be exercised when discrimination is based on a single element, or a narrow range of elements that may be used as special additives. For example, the oxides of Cr, Fe, Co, Ni, and Cu are common colorants and may not be distributed homogeneously. The distribution of Zn can also vary in glass produced by old technology. Tin (Sn) of course cannot be used to discriminate float glass.

Trace Element Distribution Trials

The glass samples comprising the window glass series G1 to G5 were indistinguishable for most elements determined with the

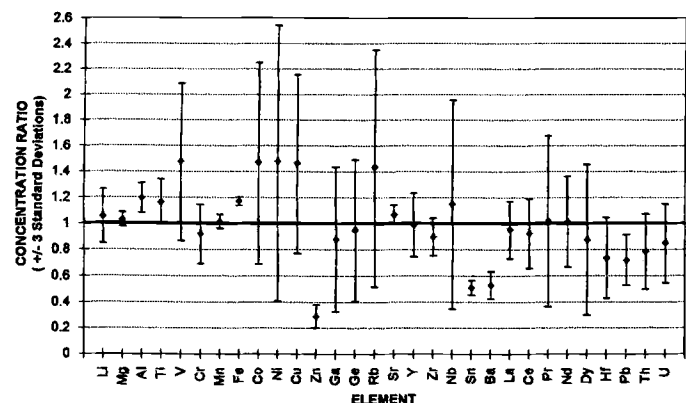


FIG. 6—Discrimination of samples 11 and 20 based on the concentration ratios of Zn and Ba.

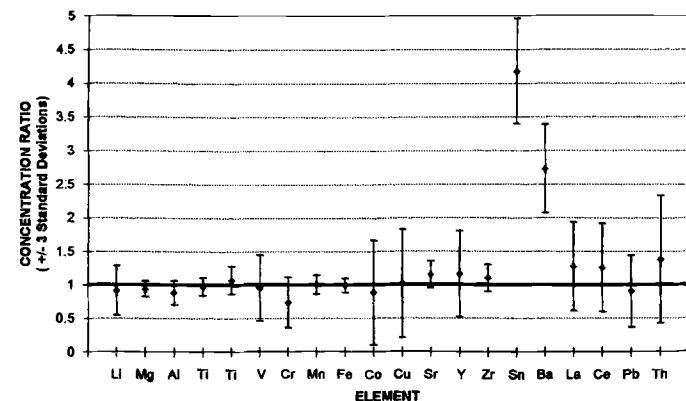


FIG. 7—Concentration ratio comparison of samples 4 and 7 showing discrimination based on Ba.

exception of Cr, Mn, Zn, As, Sr, Ba and Pb. Of these seven elements indicating differences between samples, only Cr and Zn gave ratios, which together with their three standard deviations varied by greater than $\pm 20\%$. The fluctuation of Zn was considerable in most samples, whilst Cr was higher only in one corner. These results were further supported by the quantitative data for Cr and Zn as shown in Fig. 8.

The distribution of TE in the float window glass H was exceptionally uniform. None of the determined elements showed significant variation in concentration at any of the five points sampled.

The distribution of TE in the float vehicle windscreen laminate L was also uniform across the respective sheets (LO and LI). Only indium, present at low concentration, appeared unevenly distributed. However, the ratios for Mn, Fe and Co in both sheets at the respective points of sampling showed variations in concentration suggesting differences between the two sheets of the laminate.

These differences emphasize the importance of obtaining a truly representative sample from the crime scene in order to establish both the mean and the variation in concentration of each element used for discrimination.

Evaluation

Three different proficiency testing trials provided excellent opportunities to evaluate the method.

- Three mirror glasses A, B, and C had refractive index values of 1.51750, 1.51756 and 1.51744, respectively, which suggested that B and C were different, but the situation with A was difficult to ascertain. The determination of the concentration ratios for a wide range of elements failed to discriminate A and C while the ratios for Sr and Zr showed B to be clearly different (Fig. 9). These results were further supported by the quantitative values obtained for Sr, Zr, Ba and Pb (Table 7).

- Two sets of glasses E and F had refractive index values differing by only 8 in the fifth decimal place. The concentration ratios of Mn, Zr, Ce and Pb indicated distinct differences between the two sets of samples. However, only Ce and Pb gave ratios which, including their 3 standard deviations, differed from unity by more than 20%, and thus clearly discriminated the two sets (Fig. 10).

- Three glass samples Q1, Q2 and K1 were compared using elemental ratios determined from the analysis of weighed fragments. The results in Figs. 11 and 12 show that Q2 and K1 could not be discriminated and Q1 was clearly different to the other two samples.

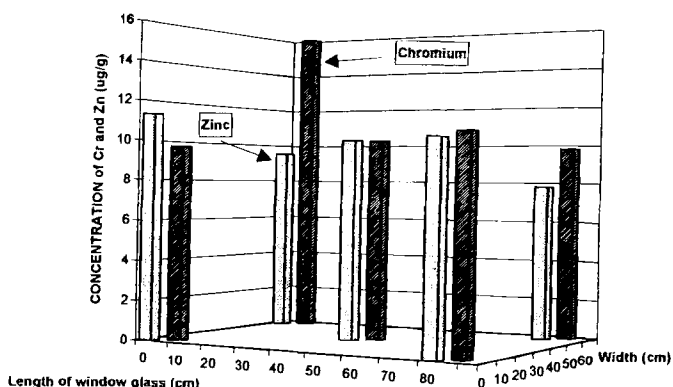


FIG. 8—Variation of Cr and Zn concentration in non-float window glass G.

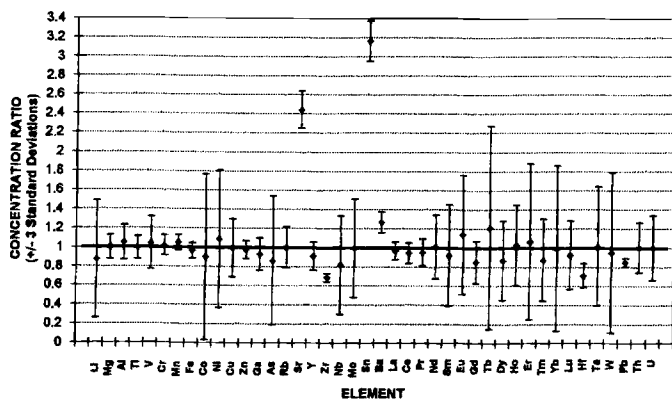


FIG. 9—Discrimination of mirror glasses A and B based on the concentration ratios of Sr and Zr.

- The analyses of Q1, Q2 and K1 were repeated using unweighed fragments each of about 1 mg in weight to simulate a casework situation. In order to obtain good counting statistics for samples of this small size, a single analysis of each sample in a final dilution volume of 2 mL was used. This reduced the number of measurements per sample from five to two and so although the results were similar to those of the weighed samples, they were less reliable.

Conclusion

ICPMS has been shown to be a sensitive, accurate and precise technique for the analysis of trace elements in glass. The three acid digestion procedure with removal of Si and residual HF and HCl provided good recovery of trace elements, and the use of 5% HNO₃ in the final solution introduced the least amount of interfering molecular species.

The HF/HNO₃ digestion procedure without removal of silicon can be used for glass samples that contain trace elements in relatively high concentrations (>10 $\mu\text{g/g}$) where the excess dilution (1:3000) can be tolerated.

Detection limits were of the order of the ng/g level in glass. Analytical precision was in the range of 1–5% RSD for most elements based on the analysis of 5 mL of a 1 mg/mL glass solution. The smallest glass fragment that could be analyzed was estimated to be of the order of 100 μg for headlamp glass and 200 μg for container and sheet glass. The minimum sample volume that can be used with the current technology available to the authors is 2 mL. When very small samples are analyzed using a 2 mL nebulization volume a corresponding loss of precision will result.

The measurement of concentration or elemental ratios provided an accurate method for comparing glass samples without determining absolute concentrations. The compilation of ratios for a large number of elements is more comprehensive and less demanding than the quantitative quest for selected “diagnostic” elements. In addition, elemental ratios are independent of mass, unaffected by drift and less affected by suppression, and they therefore offer a means for discriminating between samples when the fragment size of the glasses under comparison is too small to be weighed accurately. Furthermore, the results can be represented graphically, providing a convenient visual assessment of the comparisons.

In the comparison of a small glass fragment of unknown origin with a “control” sample suspected of being the possible source, the homogeneity of the samples under comparison must be considered. Only a limited investigation of TE distribution in glass was made in

TABLE 7—Elements determining discrimination between mirror samples.

Mirror Sample	Refractive Index		Sr, µg/g			Zr, µg/g			Ba, µg/g			Pb, µg/g		
	a	b	a	b	mean	a	b	mean	a	b	mean	a	b	mean
A	1.51750	1.51746	121	117	119 ± 6	72.2	68.3	70 ± 6	9.15	8.46	8.8 ± 1	6.31	5.82	6.1 ± 0.6
B	1.51756	1.51752	49.6	46.9	48 ± 4	106	96.4	101 ± 15	7.18	6.30	6.7 ± 1	7.40	6.85	7.1 ± 0.8
C	1.51744	1.51746	116	113	115 ± 4	69.7	67.4	69 ± 4	8.57	8.45	8.5 ± 0.5	5.74	5.75	5.7 ± 0.5

NOTE:—Mean (± 2SD).

this study. However, it was shown that even in sheet glass, which is expected to be relatively homogeneous, variations in TE concentrations are observed. This is more pronounced in older glass samples. Therefore the “control” sample must be representative of the broken portion from which the questioned fragment may have originated.

This study agrees with the findings of Zurhaar and Mullings (10) that many trace elements in Australian float glass are in the ng/g range. They also reported that the concentrations of the same elements were of the order of µg/g in USA float glasses. Glasses with these higher concentrations of trace elements can be discriminated by ICPAES alone or in combination with other techniques (4). ICPAES and ICPMS share analytical applications and multi-element characteristics but ICPMS remains unique for its sensitivity and isotope capability and is therefore the most appropriate single technique for the discrimination of glass of Australian origin in forensic science casework.

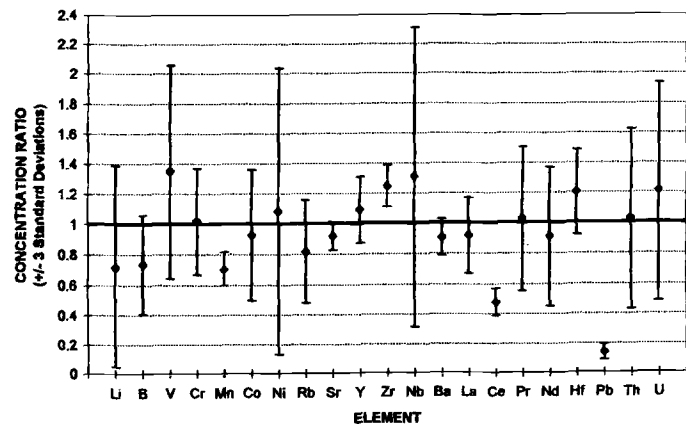


FIG. 10—Concentration ratio comparison of samples E and F showing discrimination based on Ce and Pb.

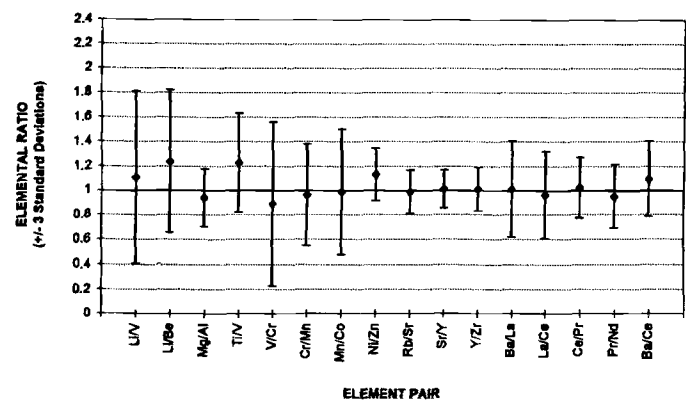


FIG. 11—Comparison of samples Q2 and K1 that could not be discriminated over a wide range of elemental ratios.

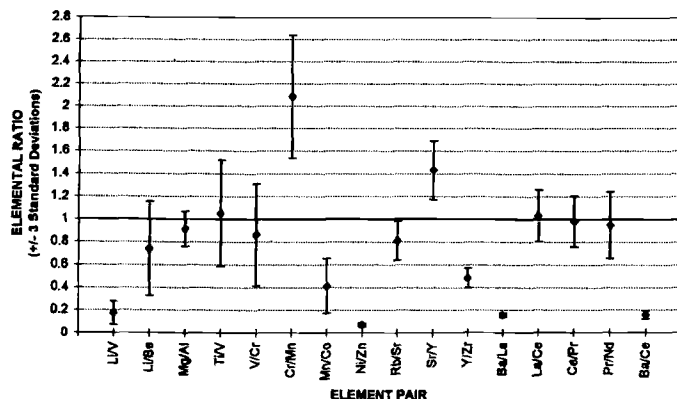


FIG. 12—Comparison of samples Q2 and Q1, which were clearly discriminated by the elemental ratios of Li/V, Cr/Mn, Mn/Co, Ni/Zn, Y/Zr, Ba/La and Ba/Ce.

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