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Statistical Discrimination of Flat Glass Fragments by Instrumental Neutron Activation Analysis Methods for Forensic Science Applications

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ABSTRACT: Instrumental neutron activation analysis (INAA) and cyclic INAA (CINAA) techniques were used for the discrimination of flat glass fragments. Employing short irradiation, delay, and count times, sample test portions of 100 μg and 1 mg (INAA) or 1 and 5 mg (CINAA) were considered. A statistical model was used to assign the elemental variation among glasses to different experimental factors; by advanced statistical methods elemental differences between specific glasses can be identified. Analysis and comparison of float glass panes produced by two major Canadian manufacturers were also performed; the two were readily differentiated, primarily on the basis of their aluminum levels.

KEYWORDS: forensic science, glass, statistical analysis, instrumental neutron activation analysis (INAA), flat glass fragments, elemental composition of flat glass

The elemental discrimination of glass samples has received considerable attention. Numerous techniques have been employed (spark source mass spectrometry [*1–3*], X-ray fluorescence [*4,5*], scanning electron microscopy [*6–8*], atomic absorption [*9–11*], dc arc emission spectrography [*12,13*], and neutron activation analysis [*14,15*]), but it now appears that inductively coupled plasma-atomic emission spectroscopy [*15–20*] is emerging as the dominant method for discrimination between glass types, including flat, container, tableware, vehicle headlight, and so on. However, despite the impressive sensitivity of the technique, its ability to discriminate among flat (window, mirror) glass samples is hampered by the low precision associated with many elements in these matrices. Reports of poor discrimination may also be attributed to the fact that much of this work was carried out in the United Kingdom on flat glass produced by a relatively limited number of manufacturers and where homogeneity would be expected to be relatively high.

Instrumental neutron activation analysis (INAA) has received little recent consideration from researchers despite many attractive features which are particularly suited for forensic science purposes. The technique is nondestructive and allows further analyses, by the same or different methods, to be performed on the same glass test portions. In addition, using nondestructive techniques also preserves the sample for presentation in court. Coupled with the nondestructive nature of the technique is a fairly straightforward

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sample treatment procedure in which the sample is simply cleaned and weighed prior to irradiation. Many elements are capable of being detected and identified with high sensitivity and selectivity because advantage can be taken of differences in both half-lives and γ-ray energies. Simultaneous detection of many elements is possible, and since most elements possess several radioactive isotopes, a choice between detecting either a short- or long-lived radionuclide is often available. Comparison of samples by means of their γ-ray spectra without the need for quantitative comparison to elemental standards is another advantage. And, finally, the fact that the technique may be automated permits high sample throughput. Often the lack of availability of nuclear reactors, the cost per analysis, and the problem of storing and handling radioactive samples after analysis are cited as disadvantages associated with the technique. In Canada, however, small pool-type nuclear reactors (SLOWPOKES) developed by Atomic Energy of Canada Limited (AECL) are located at universities across the country, where personnel trained in radiation safety are readily available. Costs for analyses performed at these facilities are competitive with rates charged by commercial laboratories.

This paper presents results for the discrimination of flat glass fragments by neutron activation analysis. Both INAA and cyclic INAA (CINAA) [*21,22*] methods of analysis were employed to study flat glass samples randomly selected from a glass population. Since relatively rapid analytical turnaround times are often important, only short irradiation, delay, and count times were considered. Also, the short irradiation times and small sample sizes used in this work allowed us to hold residual activities in the samples to sufficiently low levels that the samples could be handled safely for purposes of evidence within two days of irradiation. (The maximum radiation level for the samples studied here was less than 0.2 milliroentgens after two days.) Investigation of small sample test portion sizes was also of interest because of the difficulty in collecting large amounts of material in most forensic science situations. The need to deal with small sample sizes immediately raised concerns about the homogeneity of element distribution within these glasses.

Experimental Details

Refractive Index Measurements and Observations on 19 Glass Samples

Nineteen glass samples comprising five refractive index (RI) groups were obtained from a Royal Canadian Mounted Police (RCMP) forensic laboratory (Edmonton, Alberta). Sample presentation typically ranged anywhere from a few milligrams of crushed glass to 50 g of a complete section of glass. Thicknesses ranged between 2.8 and 6 mm. RI measurements and the classification of each glass were provided by forensic laboratory personnel. Table 1 provides general information on the various glasses. All were clear and colorless except for Sample A2, which was slightly greenish, and E2, which was "smoke" colored. Each glass in the set was subsequently observed under short-wave ultraviolet (UV) radiation in a UV light box to test for fluorescence.

Pretreatment of Glass

Large pieces of glass were placed between a double thickness of clean paper and crushed with a hammer. Portions of the original samples were further crushed using an agate mortar and pestle equipped with a Parafilm "M" cover. The resulting fragments were less than 1 mm in maximum dimension. The crushed samples were cleaned with concentrated nitric acid for 30 min. Washing of the samples with distilled-deionized water was performed three times prior to a 95% ethanol rinse. The samples were then dried in a vacuum oven between 100 and 110°C for at least 4 h. The drying was performed just prior to weighing the samples.

TABLE 1—*Physical properties, classification, and observations involving glass fragments studied in this work.*[a]

Group	n_D	Glasses in Group, No.	Glass Classification	Observations
A	1.5171	4	A1, A3, A5—flat A2—flat, safety (car window)	A2—slight greenish tinge, two pieces plus small shards A5—three pieces
B	1.5185	4	B1—tableware (tumbler) B2, B3, B4—flat	B3—crushed glass sample
C	1.5157	3	C1, C2—flat C3—flat, safety (tempered)	
D	1.5168	4	D1—flat, safety (tempered) D2, D3, D4—flat	
E	1.5191	4	E1, E3—flat E2—flat (decorative) E4—flat (windshield)	E2—"smoke" colored, two pieces E4—two glasses, laminated together and each 3 mm in thickness

[a]All glasses not indicated otherwise were provided as a single piece.

Preparation of Glass for INAA

Test portions of nominal masses 1 mg and 100 μg were taken from each glass sample for analysis by INAA. In general, the masses were within 10% of the nominal value. A Cahn gram (Model G) electrobalance, equipped with powder paper (glassine) pans, was employed to weigh out four test portions at each mass level. The test portions were then placed directly into four nitric-acid-washed 400-μL polyethylene microcentrifuge tubes which had been previously cut in half crosswise. Care was taken to avoid skin contact with the microcentrifuge tubes. These tubes were capped, heat sealed on the edges of the cap, placed in 1-mL polyethylene vials, and finally deposited in 7-mL polyethylene irradiation vials. Empty 1-mL polyethylene vials, acting solely as spacers, were placed on top of the 1-mL polyethylene vials containing the test portion already present in the irradiation vials. All analyses were performed in triplicate, with one week separating each determination to allow for decay of the various radioisotopes. One blank (polyethylene sample tube plus vials) was also analyzed daily for each sample mass level. Irradiation and counting of the various test portions were performed using a randomized block design. This prevented biasing of inferences, drawn from analysis of the data set, due to random, day-to-day fluctuations.

Preparation of Glass for CINAA

The procedure for the INAA experiment was followed except for several notable changes. Test portions of nominal masses 1 and 5 mg were taken from each glass, except those in group B, for analysis. All the test portions were weighed, then placed directly into the hollow caps of four 400-μL polyethylene microcentrifuge tubes which had previously been positioned in the tops of the tubes. Each cap was heat sealed and placed at the bottom of a 1-mL polyethylene vial. Next, each microcentrifuge tube was cut in half crosswise so that the vial was just able to be capped. This prevented lengthwise movement of the tube within the 1-mL vial. In addition, the tube was firmly seated within an indentation in the cap of the vial to prevent side-to-side movement. The vials were

then inserted into 7-mL polyethylene irradiation vials. Empty 1-mL polyethylene vials, acting solely as spacers, were placed on top of the 1-mL polyethylene vials already present in the irradiation vials. Heat sealing of the irradiation capsules was then performed. All the vials and microcentrifuge tubes were nitric acid washed; care was taken to avoid skin contact with any of the polyethylene containers.

INAA Irradiation and Counting

The irradiation and counting operations were performed at the SLOWPOKE-2 reactor facility situated on the University of Alberta campus. Irradiation involved exposing the test portions to a nominal neutron flux of 1×10^{12} neutrons cm^{-2} s^{-1} in Site No. 1 of the reactor. The irradiation, delay, and counting periods employed were respectively 4, 1, and 5 min for the 1-mg portions and 10, 1, and 10 min for the 100-μg fragments. In each case the counting period refers to live time. Sample placement was at a distance of 1 cm from the detector in a cave which had 10-cm-thick lead walls. The height of the cave was 39 cm, while the width and length were both 30 cm (internal dimensions).

All counting was carried out with a Model 20180 EG&G ORTEC (Oak Ridge, Tennessee), horizontal, closed-end, hyper-pure germanium, coaxial detector system operating at a bias supply of +3500 V. In addition, a Nuclear Data (ND)-660 multichannel analyzer, along with an EG&G ORTEC 572 amplifier (coarse gain of 20 and a shaping time of 3 μs) and an ND-575 ADC, were coupled to this unit. An EG&G ORTEC 419 precision pulse generator module (operated at 75 Hz) using a minimum rise time was also included. The detector specifications included a relative efficiency of 22.4%, a measured full-width half-maximum of 1.71 keV, and peak-to-Compton ratio of 59.3:1 for the 1332 keV photopeak of cobalt-60 (^{60}Co). All detector specifications are quoted for a 6-μs amplifier time constant. The sodium-24 (^{24}Na) (Na-1 = 1369 keV and Na-2 = 2754 keV, half-life 15.0 h), aluminum-28 (^{28}Al) (1779 keV, half-life 2.24 min) and calcium-49 (^{49}Ca) (3083 keV, half-life 8.8 min) photopeak signals were collected using a 4096 channel spectrum and were stored on floppy disks for later retrieval and analysis.

CINAA Irradiation and Counting

Irradiation involved exposing the glasses to a nominal neutron flux of 1×10^{12} neutrons cm^{-2} s^{-1} in Site No. 5 of the reactor. A recycle irradiation controller supplied by AECL commercial products was employed for the timing operations. The irradiation, delay, and counting periods were respectively 25, 4, and 25 s for the 1-mg test portions and 10, 4, and 10 s for the 5-mg test portions. In each case the counting period refers to clock time. Twelve cycles of irradiation, delay, and counting were employed in each instance.

The counting geometry included a 1-cm separation between the detector end cap and the middle of the irradiation vial. All counting was performed with an 86-cm^3 active volume EG&G ORTEC WIN-15 horizontal, closed-end, coaxial germanium(lithium) [Ge(Li)] detector system operating at a bias supply of +3500 V. In addition, an ND-660 MCA, along with an EG&G ORTEC 472A amplifier (with a coarse gain of 20, a fine gain of 9.40, and a shaping time of 1 μs) and an ND-575 ADC, were coupled to this unit. A Mech-Tronics Nuclear (Model 1000) precision pulse generator module (operated at 60 Hz) employing a minimum rise time was also included. The detector specifications included a relative efficiency of 18.5%, a measured full-width half-maximum of 2.1 keV, and peak-to-Compton ratio of 53:1 for the 1332-keV photopeak of ^{60}Co. The hafnium-179m (half-life 19 s) photopeak at 216 keV was collected using a 2048 channel spectrum. Following counting, a delay time of 4 s was allowed to elapse before the sample was reinserted into the reactor core. After the preselected number of cycles had expired,

the cumulative spectrum for twelve cycle periods was stored on floppy disks for later retrieval and analysis.

Although several other elements could be detected by CINAA, only hafnium showed sufficient variation in counts among the glasses to warrant statistical study.

Spectral Correction and Analysis

Spectral peak searching was accomplished using a software program (PREP 10) supplied by Nuclear Data. Dead times of less than 10% were maintained for each test portion. Dead-time corrections [*23,24*] for the decay of short-lived radioisotopes in the presence of active, longer-lived isotopes such as ^{24}Na and chlorine-38 (^{38}Cl), along with a correction factor for random summing effects [*25*], were calculated using an Apple Macintosh Plus computer with Microsoft Excel software and applied to the photopeaks. The data were also normalized to either correspond to 1 mg or 100 μg of material (INAA), or to 1 or 5 mg of material (CINAA). The resulting data were analyzed using the Statistical Package for the Social Sciences (SPSS-X) on the University of Alberta Amdahl mainframe computer. The program UANOVA was employed.

All comparisons between glasses were made from counting data directly rather than by running standards and converting to elemental concentrations. This saved time and reduced uncertainties.

Live Time/Dead Time Correction of Spectra from CINAA

Spyrou and Kerr [*21*] have corrected for the dead time of the detector by applying a different live time/dead time correction to each accumulated single spectrum (that is, each cycle period). After correction of the individual spectra, the resulting number of counts for each cycle was summed to obtain the cumulative detector response. For this investigation, the cumulative detector response for the hafnium photopeak after twelve cycle periods was multiplied by an overall correction factor, calculated using the cumulative clock and live times. The results obtained using this method were found to be in excellent agreement with the method of Spyrou and Kerr (the maximum difference between the two methods was 0.2%) when ten glasses representing the four refractive index groups (test portion range = 1 to 5 mg) were studied. As a result, the collection and correction of each individual spectrum prior to obtaining the cumulative detector response was considered unnecessary.

Homogeneity Investigations

Clear and colorless panes of glass were obtained from Pittsburgh Plate Glass Canada and AFG Glass Inc. The six Pittsburgh sample panes (n_D = 1.5185) were approximately 45 by 62 cm, with each pane being representative of a one- or two-month interval between production times. Two panes were nominally 2 mm in thickness; an additional two panes were nominally 3 mm, one was 5 mm, and the last was 6 mm thick. The four AFG panes (n_D = 1.5168) were approximately 38.5 by 61 cm with nominal thicknesses of 2 and 4 mm for each of two panes. A 29-day interval existed between production times for sample panes of the same thickness.

The four corners of each pane were removed using a tungsten carbide wheel cutter and stored separately. Pretreatment and test portion preparation were performed as outlined above for each study (INAA and CINAA). Only one test portion, however, was removed from each corner at the two mass levels (1 mg and 100 μg or 1 and 5 mg). Irradiation and counting, along with spectral correction of the various test portions, also followed the experimental procedures described above.

Results and Discussion

Detection of Float Glass

Observation of the glasses under shortwave UV irradiation was performed because tin contact surfaces, resulting from the possible float glass production process, have been reported to exhibit a yellowish fluorescence [*26*]. Several of the glasses exhibited a strong yellowish fluorescence (A1, A2, A3, B2, B4, D2, D4, E2, E3, and E4). This was taken as evidence of float glass production, since panes of glass known to be manufactured by the float glass process exhibited similar strong fluorescence. In contrast, the fluorescence displayed by the remaining glasses was much less intense; their method of production, therefore, could not be conclusively identified.

Statistical Evaluation of Data Sets

An example of the raw data, obtained as described in the Experimental Details section, is shown in Table 2. The data were subjected to several types of statistical analysis.

The *F*-test is employed routinely for the comparison of three or more averages. Employing this test, the variance between different data sets, compared with the variance found within these sets, may be assessed, and the probability that the various samples have a common mean may be determined. However, to find out which mean differences are discernible requires the performance of multiple comparisons tests. Although paired ("pairwise," often used by statisticians) multiple comparisons are simple to perform, it is important to recognize that the specified Type I error (α) is applicable to every comparison studied. As a consequence, if several paired multiple comparisons are performed in the analysis of an experiment, the chance of making a Type I error in any of the comparisons becomes substantial. A better approach to this problem is to use an experimental ("experimentwise," often used by statisticians) error rate to ensure that the chance of making any Type I error in the total number of comparisons required for an experiment will not be above a specified level. Under these conditions the tests performed will be somewhat insensitive (that is, conservative) to differences between individual means (paired comparisons), since the error rate for each individual comparison will only be a fraction of the overall experimental error rate. Tukey's alternate multiple comparisons procedure (Tukey B) [*27*] is an example of a procedure which uses an experimental error rate, while the least statistically discernible difference [*28*] (sometimes referred to as the least significant difference or LSD) method employs a paired error rate.

The Overall Statistical Model

The overall statistical model for the glasses in this investigation may be represented as a linear combination of several population treatment effects.

$$Y = \eta + \text{glass} + \text{size} + \text{size} * \text{glass} + \text{test portion} + \text{size} * \text{test portion} + \text{repeat} + \text{size} * \text{repeat} + \text{error} \quad (1)$$

where Y is a response function or matrix consisting of the levels of the elements found in a particular glass. The grand mean, η, and the treatment and interaction terms are also column vectors. (The interaction terms are identified by an asterisk between the components of the terms.) If the grand mean is considered an origin, then deviations from this origin are represented by the remaining terms of the model. The random error term designates the cumulative effect of other variables that may be unknown to the experimenter or are very small in magnitude and as such do not appear as separate identifiable entities in the model. It also includes the uncertainty resulting from statistical

TABLE 2—*Example of data collected by INAA for four 1-mg and four 0.1-mg test portions of a single flat glass (Sample A1).*[a]

Test Portion	Date	Raw Counts				Background Counts[b]				Pulser[c]		Background[d]		Clock Time, s[e]	Mass, mg
		Na-1	Na-2	Al	Ca	Na-1	Na-2	Al	Ca	Count 1	Count 2	Count 1	Count 2		
Al-3	27 Oct. 1987	14 167	7182	28 551	558	2213	216	1221	76	21 796	21 423	0	132	315.6	0.9729
	3 Nov. 1987	14 130	7047	27 264	518	2179	366	1108	185	21 783	21 423	3	120	315.2	0.9729
	10 Nov. 1987	13 996	7031	27 331	523	1904	248	1075	210	21 788	21 403	0	108	315.0	0.9729
Al-4	27 Oct. 1987	13 578	6763	26 600	598	2542	194	1030	32	21 796	21 436	0	83	314.8	0.9728
	3 Nov. 1987	14 207	6965	27 599	582	2108	355	903	66	21 783	21 440	3	81	315.2	0.9728
	10 Nov. 1987	13 774	7059	27 740	574	2135	223	1125	171	21 788	21 472	0	85	315.3	0.9728
Al-5	19 Nov. 1987	14 356	7201	27 719	566	2198	270	927	181	21 846	21 424	0	94	315.6	0.9688
	5 Nov. 1987	14 005	6996	27 037	545	2228	182	1107	95	21 792	21 415	0	115	315.2	0.9688
	12 Nov. 1987	13 695	6937	27 094	513	2340	250	935	181	21 771	21 424	9	105	315.1	0.9688
Al-6	29 Oct. 1987	14 375	7234	27 878	548	3341	220	918	55	21 779	21 416	1	85	315.5	0.9750
	5 Nov. 1987	14 079	7115	27 842	567	2083	219	825	112	21 792	21 408	0	116	315.3	0.9750
	19 Nov. 1987	13 914	7055	26 835	550	2076	171	968	162	21 846	21 494	0	147	315.2	0.9750
Al-9	27 Oct. 1987	7 296	3671	5 183	192	584	68	375	36	43 591	43 418	0	16	609.0	0.1014
	3 Nov. 1987	7 870	3822	5 171	198	756	168	285	50	43 566	43 424	6	44	609.2	0.1014
	10 Nov. 1987	7 236	3733	5 025	206	595	68	357	28	43 575	43 392	0	63	608.8	0.1014
Al-10	27 Oct. 1987	7 333	3610	5 131	206	564	121	328	61	43 591	43 594	0	4	608.9	0.0957
	3 Nov. 1987	7 324	3698	4 798	195	1001	81	356	44	43 566	43 438	6	32	608.7	0.0957
	10 Nov. 1987	6 802	3379	4 761	166	759	126	204	0	43 575	43 450	0	50	608.2	0.0957

Al-11	29 Oct. 1987	6 465	3214	4 765	197	680	9	615	8	43 558	43 401	2	22	608.5	0.0924
	5 Nov. 1987	6 921	3370	4 724	181	688	155	531	12	43 583	43 427	0	54	608.9	0.0924
	19 Nov. 1987	6 464	3327	4 877	190	642	310	270	9	43 692	43 521	0	27	608.5	0.0924
Al-12	19 Nov. 1987	6 740	3488	4 843	163	732	110	252	21	43 692	43 542	0	26	608.5	0.0904
	5 Nov. 1987	7 272	3561	4 837	191	568	96	308	32	43 583	43 420	0	20	608.8	0.0904
	12 Nov. 1987	6 617	3369	4 661	171	798	109	394	18	43 542	43 440	18	31	608.2	0.0904
Bl-R	27 Oct. 1987	120	54	289	0	32	0	38	0	21 796	21 783	0	0	301.8	
	3 Nov. 1987	60	35	292	0	149	0	14	0	21 783	21 758	3	0	301.8	
	10 Nov. 1987	21	0	322	0	9	0	12	0	21 788	21 769	0	0	301.8	
Bl-T	29 Oct. 1987	114	28	156	0	14	0	54	0	21 779	21 756	1	3	301.8	
	5 Nov. 1987	161	105	220	0	145	5	32	0	21 792	21 779	0	0	301.9	
	12 Nov. 1987	175	72	210	0	9	0	58	0	21 771	21 750	9	2	301.8	
Bl-S	27 Oct. 1987	76	26	501	0	36	0	32	0	43 591	43 545	0	0	604.6	
	3 Nov. 1987	291	170	540	0	83	4	102	0	43 566	43 539	6	0	604.5	
	10 Nov. 1987	105	60	468	0	84	0	80	0	43 575	43 559	0	0	604.3	
Bl-U	29 Oct. 1987	503	246	426	0	114	12	78	0	43 558	43 472	2	15	604.9	
	5 Nov. 1987	412	212	461	3	157	5	95	0	43 583	43 524	0	4	604.8	
	12 Nov. 1987	233	102	399	0	182	33	77	0	43 542	43 452	18	10	604.6	

[a]Each portion was irradiated and counted three times at approximately one-week intervals. Included are triplicate measurements on four blanks (Bl-R through Bl-U).

[b]Counts underlying the photopeaks.

[c]Average of pulser counts without (Count 1) and with (Count 2) the glass test portion in the detector cave.

[d]Background counts associated with the two pulser peaks.

[e]Clock times for live times of either 300 or 600 s.

counting error; in some instances this may be a major part of the total random error. The size and glass effects may be regarded as fixed effects since only distinct levels are tested, while the test portion chosen and the repeated measurements are considered as being taken randomly from a particular distribution.

Data Analysis Using the Overall Statistical Model

Analysis of the glass data was performed using the King-Henderson algorithm [29] as the mean square model. Results of the variance analysis for one of the five RI groups studied by INAA are presented in Table 3, while Table 4 provides a summary of *F*-ratios for the four RI groups studied by CINAA. In each case the grand mean, excluded from these tables, showed evidence of a nonzero value. Investigation of the size and interaction effects was not pursued because in practice comparable test portion sizes would be employed. Note that, even though the number of counts contained in a photopeak may

TABLE 3—*Multivariate and univariate* F-*ratios, degrees of freedom and probability values for the glass and test portion terms of the overall statistical model (A group,* $n_D = 1.5171$*).*

Hypothesis term: glass
Error term: test portion (glass)

MULTIVARIATE *F*-RATIOS

Test	*F*-Ratio	DFH	DFE	Probability
Pillais criterion	3.804	12.000	33.000	0.001
Hotellings trace	243.89	12.00	23.00	0.00
Wilk's lambda	27.7644	12.0000	24.1033	0.0000

UNIVARIATE *F*-RATIOS

Variable	*F*-Ratio	DF1	DF2	Probability
Na-1	5.51	3	12	0.0130
Na-2	6.13	3	12	0.0091
Al	901.10	3	12	0.0000
Ca	13.85	3	12	0.0003

Hypothesis term: test portion (glass)
Error term: repeat (test portion, glass)

MULTIVARIATE *F*-RATIOS

Test	*F*-Ratio	DFH	DFE	Probability
Pillais criterion	0.743	48.000	128.000	0.879
Hotellings trace	0.76	48.00	110.00	0.86
Wilk's lambda	0.7512	48.0000	113.7497	0.8674

UNIVARIATE *F*-RATIOS

Variable	*F*-Ratio	DF1	DF2	Probability
Na-1	0.81	12	32	0.6350
Na-2	1.45	12	32	0.1956
Al	0.57	12	32	0.8474
Ca	0.48	12	32	0.9091

TABLE 4—*Univariate* F-*ratios, degrees of freedom, and probability values for the glass, test portion, and repeat terms of the overall statistical model (A group,* n_D *= 1.5171, C group,* n_D *= 1.5157, D group,* n_D *= 1.5168, and E group,* n_D *= 1.5191).*

Hypothesis term: glass
Error term: test portion (glass)

UNIVARIATE *F*-RATIOS FOR Hf

RI Group	*F*-Ratio	DF1	DF2	Probability
A	34.90	3	12	0.0000
C	649.79	2	9	0.0000
D	27.39	3	12	0.0000
E	2.07	3	12	0.1571

Hypothesis term: test portion (glass)
Error term: repeat (test portion, glass)

UNIVARIATE *F*-RATIOS FOR Hf

RI Group	*F*-Ratio	DF1	DF2	Probability
A	3.67	12	32	0.0016
C	2.56	9	24	0.0318
D	1.18	12	32	0.3362
E	4.19	12	32	0.0006

Hypothesis term: repeat (test portion, glass)
Error term: sixe * repeat (test portion, glass)

UNIVARIATE *F*-RATIOS FOR Hf

RI Group	*F*-Ratio	DF1	DF2	Probability
A	1.22	32	32	0.2896
C	0.70	24	24	0.8022
D	1.24	32	32	0.2758
E	0.63	32	32	0.9030

not be due entirely to one element owing to interfering reactions [for example, $^{28}Si(n, p)^{28}Al$, $^{24}Mg(n, p)^{24}Na$, and $^{27}Al(n, \alpha)^{24}Na$], comparisons among glasses are not affected because the composite photopeaks and the information contained in them provide a characteristic pattern determined by the elements present in a particular glass. This is an additional advantage to the direct use of counting data in place of conversion to elemental concentrations.

For the INAA study, multivariate and univariate *F*-test analyses provide an efficient way of determining which multiple comparisons should be studied in greater detail. The glass term (multivariate comparisons), showed strong evidence (that is, a probability value of approximately zero) for a difference in the elemental composition of the Group A glasses. This was also true for the other RI groups. Univariate *F*-ratios aided in determining whether these differences in mean vectors were attributable to influences from all three elements, or whether certain elements appeared to contribute as a result of correlation. In Group A, for example, Na-2, Al, and Ca all contribute to the differences noted among glasses.

In each of the RI groups there was no evidence from either multivariate or univariate procedures to suggest the existence of a statistically discernible difference in the population means for any of the elements when the test portion and repeat terms were investigated. Specifically, the test portion term indicated "local" homogeneity for the elements sodium, aluminum, and calcium, where "local" acknowledges that only glass fragments with small dimensions were studied. The one exception was the aluminum *F*-ratio for the test portion term (Group D), which had a probability value of 0.0096. This suggested that not all of the test portions from a particular glass could be viewed as being indistinguishable from one another. However, since the probability value was very close to the 1% significance level, further study of the glasses in Group D (that is, more data) would be warranted. The repeat term, on the other hand, indicated that the variability associated with the measurement technique did not discernibly assist in the discrimination of glasses within the same RI group.

The glass term (CINAA study) indicated strong evidence for a statistically discernible difference in the hafnium levels of at least one glass within each of Groups A, C, and D. All of the glasses in Group E were found to possess similar hafnium levels. Analysis of the test portion term revealed that further study of the glasses in Group A (that is, more data) would be necessary to determine definitely whether the hafnium values for certain test portions were actually discernible from other test portions taken from the same glass. However, since the probability value for the test portion term (0.0006) for the E group glasses was quite small, there was strong evidence to support the idea of an inhomogeneous distribution of hafnium within these glasses. Therefore, a number of test portions should be used in any analysis involving the E glasses to obtain a more reliable estimate of the levels of hafnium. Finally, none of the glasses showed evidence of a difference in their elemental mean responses when the repeat term was considered.

Paired comparisons of the various glasses found within an RI group were undertaken using Tukey's alternate multiple comparisons procedure (Tukey B). The hypothesis term for the comparisons was size * glass, and an experimental error rate of 0.01 was employed. Since the model equation for the Tukey B procedure was size * glass, this represented a fixed effects model. Coupling of this fixed effects model with a balanced design (that is, equal sample sizes) meant that the statistical tests in this section were reasonably insensitive to deviations from the homogeneity of variance assumption [*30*]. This is important because analyses where one or the other of these conditions is not present must account for the possibility of heterogeneous variances whenever a pooled variance term is utilized. Failure to account for this heterogeneity of variance may result in a situation where the Type I error is dramatically increased beyond the level to which an experimenter believes it is controlled.

Results of the multiple comparisons for Group A appear in Table 5 (INAA study); Table 6 contains the results for the CINAA investigation. The quoted probabilities are for the LSD procedure (paired error rate) and constitute a limitation of the program UANOVA. Although the probability values obtained in this manner are not absolutely correct, the two methods agree on which comparisons resulted in statistically discernible outcomes. Overall, at the 1-mg level 90% of all the paired comparisons between glasses of the same RI are able to be distinguished when a 1% experimental error rate is employed. "Distinguished" is used, here, in the sense that two glasses are deemed distinguishable when a paired comparison results in a probability value of 0.01 or less for at least one of the elements. At the 100-μg level, 73% of all the paired comparisons are distinguishable. The differences are generally quite marked, with probability values of less than 1 in 10 000 being common. Aluminum was found to be the best discriminating element, followed by sodium and then calcium. For the hafnium data, 33% of all the paired comparisons between glasses possessing the same RI were distinguishable at the 1-mg test portion level when a 1% experimental error rate was employed. This rose to 52% at the 5-mg test portion level.

TABLE 5—*Tukey B procedure for paired comparisons of the A glasses using four 1-mg or four 100-μg test portions of each glass.*

	Tukey B Probability Values	
	100-μg Test Portions	1-mg Test Portions
Na-1 comparison		
A1 *vs* A2	NSD[a]	NSD
A1 *vs* A3	NSD	NSD
A1 *vs* A5	NSD	*[b]
A2 *vs* A3	NSD	NSD
A2 *vs* A5	NSD	*
A3 *vs* A5	NSD	*
Na-2 comparison		
A1 *vs* A2	NSD	NSD
A1 *vs* A3	NSD	NSD
A1 *vs* A5	NSD	**[c]
A2 *vs* A3	NSD	NSD
A2 *vs* A5	NSD	*
A3 *vs* A5	NSD	**
Al comparison		
A1 *vs* A2	***[d]	***
A1 *vs* A3	NSD	***
A1 *vs* A5	*	***
A2 *vs* A3	***	***
A2 *vs* A5	***	***
A3 *vs* A5	***	***
Ca comparison		
A1 *vs* A2	NSD	NSD
A1 *vs* A3	NSD	NSD
A1 *vs* A5	NSD	**
A2 *vs* A3	NSD	NSD
A2 *vs* A5	NSD	***
A3 *vs* A5	NSD	***

[a]NSD = Not statistically discernible.
[b]* = $0.001 <$ probability < 0.01.
[c]** = $0.0001 <$ probability < 0.001.
[d]*** = probability < 0.0001.

Glass B1 was the only glass in this study not classified as flat glass. Comparison of B1 to the other glasses indicated distinctive Ca and Al values, with the highest average count values for the 19 glasses at both test portion sizes. These elevated values appear to parallel levels found in cheaper transparent tableware glass, which has practically the same composition as container glass [*31*]. Typical values for calcium oxide (CaO) in container glass range from 9.6 to 11.5%, and in modern flat glass from 7 to 10% CaO [*32,33*].

Of the remaining 18 flat glasses, glasses A1, A2, A3, B2, B4, D2, D4, E2, E3, and E4 were of particular interest because their intense fluorescence suggested that they might have been produced by the float glass process. At the 1-mg level, the A glasses were readily distinguished from one another based on their aluminum content, the B glasses were easily discerned based on their sodium values, and the E glasses were readily discriminated by their aluminum values. Only glasses D2 and D4 could not be distinguished by their Na, Al, and Ca values. When the results for the 100-μg level were considered, the paired comparisons (A1, A3), (B2, B4), (D2, D4), and (E3, E4) were not statistically discernible.

Hafnium does not appear to be a good element for the discrimination of float glasses.

TABLE 6—*Tukey B procedure for paired comparisons of the A, C, D, and E glasses using four 1-mg or four 5-mg test portions of each glass.*

Hf Comparison	Tukey B Probability Values	
	1-mg Test Portions	5-mg Test Portions
A1 *vs* A2	NSD[a]	***[d]
A1 *vs* A3	NSD	*
A1 *vs* A5	*[b]	***
A2 *vs* A3	NSD	*
A2 *vs* A5	NSD	*
A3 *vs* A5	*	***
C1 *vs* C2	NSD	NSD
C1 *vs* C3	***	***
C2 *vs* C3	***	***
D1 *vs* D2	*	***
D1 *vs* D3	**[c]	***
D1 *vs* D4	**	***
D2 *vs* D3	NSD	NSD
D2 *vs* D4	NSD	NSD
D3 *vs* D4	NSD	NSD
E1 *vs* E2	NSD	NSD
E1 *vs* E3	NSD	NSD
E1 *vs* E4	NSD	NSD
E2 *vs* E3	NSD	NSD
E2 *vs* E4	NSD	NSD
E3 *vs* E4	NSD	NSD

[a]NSD = Not statistically discernible.
[b]* = 0.001 < probability < 0.01.
[c]** = 0.0001 < probability < 0.001.
[d]*** = probability < 0.0001.

Only the A glasses were distinguishable from one another using Tukey's procedure when 5-mg test portions were considered. It was also found that no additional discrimination of the 15 glasses considered in the CINAA study was provided by hafnium when results were compared with the Na, Al, and Ca data.

Two sodium photopeaks were studied throughout the above analyses. It appears from the data in this investigation that no apparent difference exists between the information provided by the two photopeaks despite their location in different parts of the γ-ray spectrum and the considerably different background values associated with each. Therefore, in further studies only one or the other sodium photopeak need be considered. The choice may be made on the basis of possible spectral interference with one or the other by another nuclide, or on convenience when measuring the spectra.

Analysis of Float Glass Panes

For each of the test portion levels (1 mg and 100 μg), the various panes produced by a given manufacturer were found to be homogeneous for Na, Al, and Ca when within-pane (using the Studentized range test at a 10% significance level) and between-pane (using ANOVA tables at a 5% significance level) comparisons were performed. The same results were obtained for hafnium when 1 and 5-mg test portions were considered. Since the panes were produced at different times from different batches, this homogeneity also suggested a stable or consistent supply of raw materials, along with reliable control of the production process.

The results for measurements on glasses from each manufacturer appear in Table 7. In each case the results reported are an average for all the analyses performed on the glass panes studied. This corresponds to 16 measurements (4 measurements on each of 4 panes) for the AFG-produced glass and 24 (4 measurements on each of 6 panes) for the Pittsburgh-produced glass. For both mass levels a statistically discernible difference in the aluminum content of the glasses was noted (that is, the probability that glasses from the two manufacturers possess the same mean aluminum level is less than 1 in 10 000). Comparison of the counts shows the Al content of the AFG glass to be approximately double that of the Pittsburgh glass. A statistically discernible difference (that is, a probability value of 0.003) in the calcium levels was also found for 1-mg test portions. No statistically discernible difference was noted at the 1% significance level for Na and Hf at either test portion size. Testing of the average elemental values for each manufacturer was performed using a *t*-test of the difference between two means and employed a weighted average of the variances.

For the sets of 16 and 24 fragments, a % relative standard deviation (RSD) (1-mg test portions) of 1.2% (Na-1) was obtained for the AFG-produced glass, while a value of 2.2% was obtained for the Pittsburgh-produced glass. The Na-2, Al, and Ca values for the AFG (Pittsburgh) glasses were respectively 1.8 (2.5), 1.7 (3.6), and 4.2 (5.5) %. At the 100-μg level these values rose slightly in general, and attained values of 2.1 (2.4), 2.4 (2.6), 3.4 (11.8), and 5.5 (8.8)% for Na-1, Na-2, Al, and Ca, respectively. A % RSD of 25.1 and 17.1% were obtained for the AFG- and Pittsburgh-produced panes at the 1-mg level. These values decreased to 16.8 (AFG) and 14.7% (Pittsburgh) for 5-mg test portions.

Summary

INAA and CINAA have been applied to study the discrimination of flat glass fragments randomly selected from a glass population. In general, elemental heterogeneity was noted between the glasses, while no evidence was found to suggest the presence of heterogeneity

TABLE 7—*Results for flat glass samples from two major Canadian manufacturers.*[a]

	Manufacturer	
Elements	AFG	Pittsburgh
	100-μg Test Portions	
Na-1	7 347	7 480
Na-2	3 717	3 759
Al	5 152	2 626
Ca	212	213
	1-mg Test Portions	
Na-1	14 771	14 970
Na-2	7 413	7 534
Al	29 201	12 765
Ca	610	644
Hf	2 370	2 786
	5-mg Test Portions	
Hf	2 153	2 689

[a]The reported values are average counts for a total of 16 analyses on 4 AFG-produced panes or 24 analyses on 6 Pittsburgh-produced panes.

within any of the data sets when the analytical variance (repeat term of the overall statistical model) was studied. The sodium, aluminum, and calcium data revealed, in general, no evidence of elemental heterogeneity within a glass when test portions as small as 100 μg were considered. This was not true, however, for hafnium.

When a 1% experimental error rate was employed, 90% of all paired comparisons between glasses possessing the same refractive index (Na, Al, and Ca data) were distinguishable when 1-mg test portions were analyzed, while at the 100-μg level a discrimination rate of 73% was attained. For the hafnium data set, 33% of the paired comparisons were distinguishable at the 1-mg test portion level; this rose to 52% for 5-mg portions. Aluminum was found to be the best discriminating element in the glasses studied here. No evidence was found to suggest the presence of elemental heterogeneity within the glasses produced by either of two Canadian manufacturers, but a statistically discernible difference was noted between glass compositions for the two manufacturers.

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