Journal of Radioanalytical Chemistry, Vol. 15 (1973) 367—388

COMPARISON OF GLASS FRAGMENTS BY NEUTRON ACTIVATION ANALYSIS

R. F. COLEMAN, G. C. GOODE

Atomic Weapons Research Establishment, Aldermaston, Berks. (England)

A method of comparing glass fragments of potential application to forensic science has been developed and evaluated. A representative sample of window glass from England and Wales has been collected and analysed for about 25 elements. An automated radiochemical separation followed by gamma-spectroscopy was used in order to determine the concentration of the maximum number of elements. Frequency distributions of the elemental concentration are shown and used to assess the discrimination of the technique and compare it with the measurement of refractive index. A few simulated cases have been included to demonstrate the possible application to forensic science problems.

Introduction

At the First International Conference on Forensic Activation Analysis in San Diego some very preliminary results on the comparison of glass fragments was reported. Since that time work has continued on this topic using neutron activation techniques at AWRE Aldermaston although in the last two years the effort has been intermittent.

This paper assesses the evidential value of multi-element analysis using activation techniques, however, in this study emphasis was placed on obtaining data on as many elements as possible so that if either activation analysis, mass spectrometry or emission spectroscopy were used for case samples then most of the necessary background information would be available for presentation in court. To date, elemental analysis of glass has been used in only a few cases, further development of the activation procedure to facilitate its use in routine case work is now in progress.

Experimental

Assessment of the evidential value of multi-element analysis

A preliminary assessment of glass comparison techniques by Coleman and Wood[1] showed that multi-element analysis has considerable potential for glass. It was therefore decided to use the statistical evaluation developed by Parker[2] as a quantitative method of assessment and for comparison with existing methods. The essential requirements for this method of assessment are: (a) the collection of a representative sample of the glass population of interest, (b) development of a reliable method of analysis with consistent experimental errors for each type of glass, (c) analysis of the representative sample of glass to determine the frequency distribution of element concentration.

Collection of representative sample

It is not realistic to regard glass as a single homogeneous commodity because of the marked difference in composition for different types of glass. As window glass features most frequently in forensic science investigations, it was decided to concentrate on that type and various techniques for collecting a representative sample of window glass from England and Wales were considered. The preferred method was to collect samples of broken window panes from the scenes of fires with the aid of the local Fire Brigade Officer throughout the country. The incidence of fires is considered to be sufficiently random for our purpose and this approach also provides ready access to additional useful information concerning the building from which the samples originate. From over 900 samples collected in this way, a suitable stratified group of 540 samples were selected on the basis of the population served by each brigade.

Criticism of the method of sampling might be made on the grounds of the risk of fires in old buildings will be greatest and hence lead to a non-representative sample. There is in fact no direct evidence for this from fire statistics as shown by the recent investigation by Miles[3] using the data for fires in private dwellings in 1963. This independence of fire risk has been confirmed for the survey samples by comparison with building statistics for dwellings for the past 150 years. It might also be expected that some physical damage of glass samples could result from the heat of the fire and for this reason fire officers were entrusted to select samples from as far away from the source of the fire as possible.

Development of an analytical procedure

The major factors limiting the number of elements determined and the analytical error attainable by neutron activation of glass are (1) the large quantity of ^{24}Na produced and (2) the complexity of the induced gamma-spectra. These problems can be partially resolved by the use of radiochemical separations or high resolution gamma-spectroscopy.

When the choice was made a few years ago large germanium detectors were not available and the smaller detectors were not sufficiently sensitive for the analysis of small samples in a reasonable time. A radiochemical separation based upon the sequential solvent extraction of 25 elements as six groups of neutral chelates has been developed, the system being fully automated to enable large numbers of samples to be handled. Full details of the technique employed have been described by Goode et al.[4] and only a brief description will be presented here.

Fig. 1 shows an overall view of the equipment developed for automated radiochemical separation with comprises a pair of solvent extraction cells, a fraction collector and reagent dispensing system. The entire sequence of analytical operations involved in the separation scheme, performed after the samples of irradiated glass have been dissolved and manually transferred to the cells, is controlled by a multi channel electronic programmer developed at AWRE[3] and now available commercially.* The programmer is controlled by a series of variable frequency pulses from a magnetic tape, these having been recorded by first manually operating the system as required. Briefly the solvent extraction technique involves stirring the aqueous phase and heavier organic phase containing the chelating agent in glass cell (Fig. 2) and allowing the phases to separate out. The lower phase containing the extracted ions is run off by opening a relay-operated valve, this being closed immediately the phase boundary bridges a pair of platinum electrodes sealed into the lower part of the cell. These are arranged to detect the difference in conductivity between the phases. With suitable intermediate washing of the remaining organic phase with pure solvent the apparatus completes three extraction steps for each group. The separation scheme used is illustrated diagrammatically in Fig. 3. The aqueous glass solution obtained by dissolution in hydrofluoric and perchloric acids is retained in the solvent extraction cell throughout while five groups of elements are sequentially extracted with suitable complexing agents under various pH conditions. The aqueous raffinate is finally removed as a sixth group which is allowed to stand for a further five days before gamma-spectrometry. Figs 4 and 5 illustrate the simplification of spectra which results from radiochemical group separation. In Fig. 4 are shown gross gamma-spectra obtained for a sample of modern window glass after 5 days irradiation at a neutron flux of $2 \cdot 10^{12}$ n $\cdot$ cm^{-2} $\cdot$ sec^{-1} followed by 4 and 12 days cooling respectively. It can be seen that after 4 days decay ^{24}Na activity predominates obscuring other elements completely. After a further 7 days a complex spectrum with contributions from over 20 elements is observed. Although resolution of this spectrum is possible by least squares fitting procedures using a large number of standards errors occur in the estimation of minor constituents and a considerable amount on analytical information is lost due to the long decay period. In Fig. 5 are shown the relatively simple individual group spectra for the same glass sample which can be resolved using a relatively small number of standards in each case.

In addition to the long irradiation and radiochemical separation, very useful additional elements can be determined, i.e. aluminium, manganese and sodium with excellent precision by gamma-counting with a sodium iodide detector 2, 10 and 60 min after the end of a 1 min irradiation ($5 \cdot 10^{12}$ n $\cdot$ cm^{-2} $\cdot$ sec^{-1}).

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*Joyce Loebl Ltd., Gateshead.

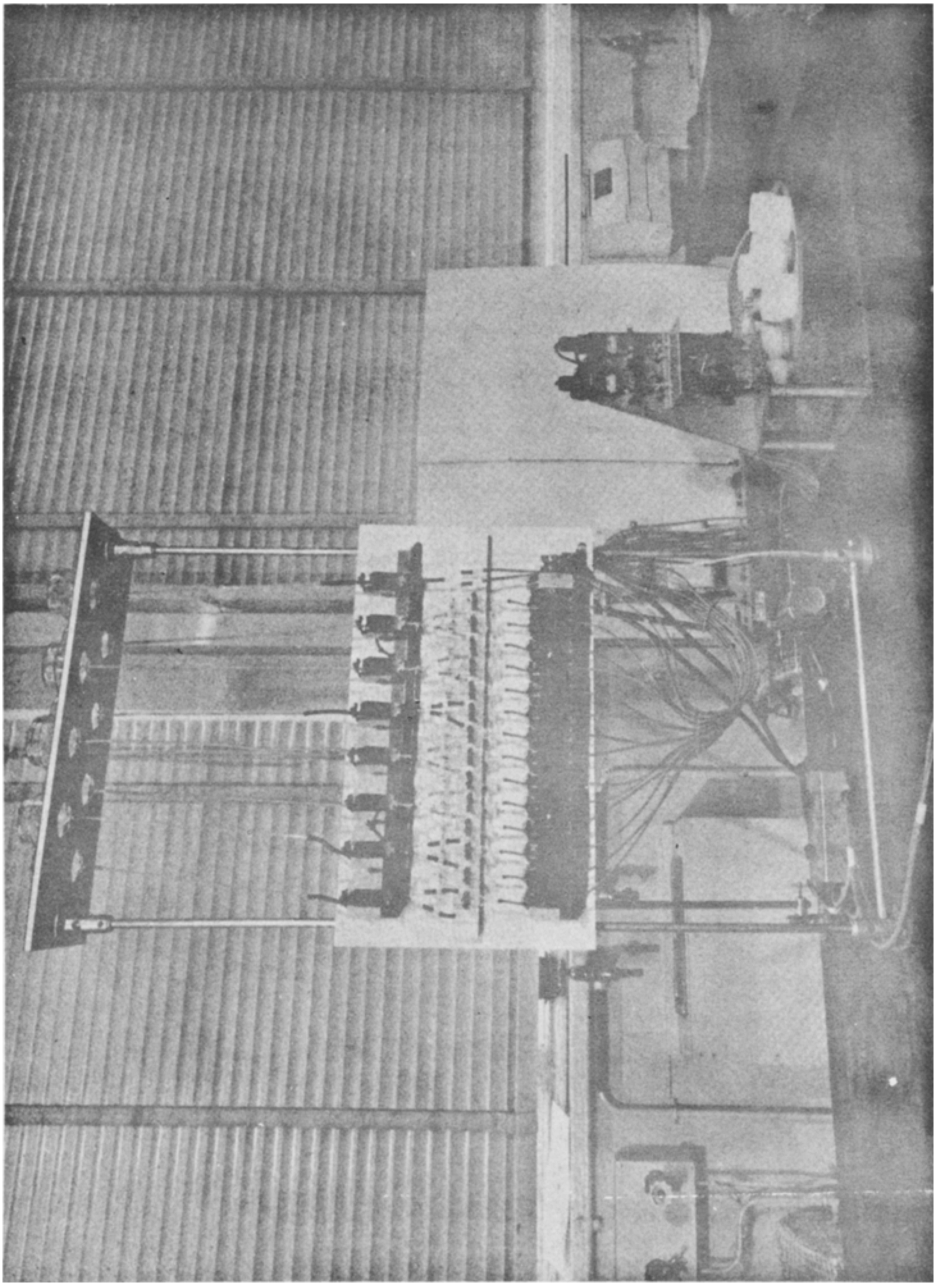

Fig. 1. Automated apparatus for radiochemical group separation

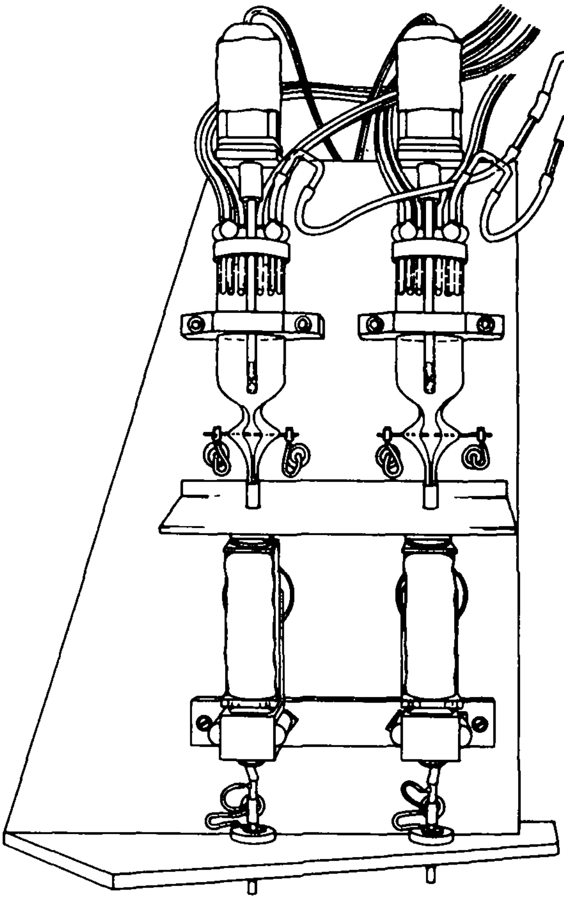

Fig. 2. Solvent extraction cells

Results

Frequency distributions of multi-element concentrations

Analytical data for Al, As, Ba, Ca, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Mg, Mn, Na, Rb, Sb, Sm, Sr, Th and Yb were obtained for the 539 survey samples by the methods described. In addition the concentration of uranium in each sample was determined by a delayed neutron technique, specific for that element but requiring a separate 100 mg sample for analysis. Distribution curves for the concentration of

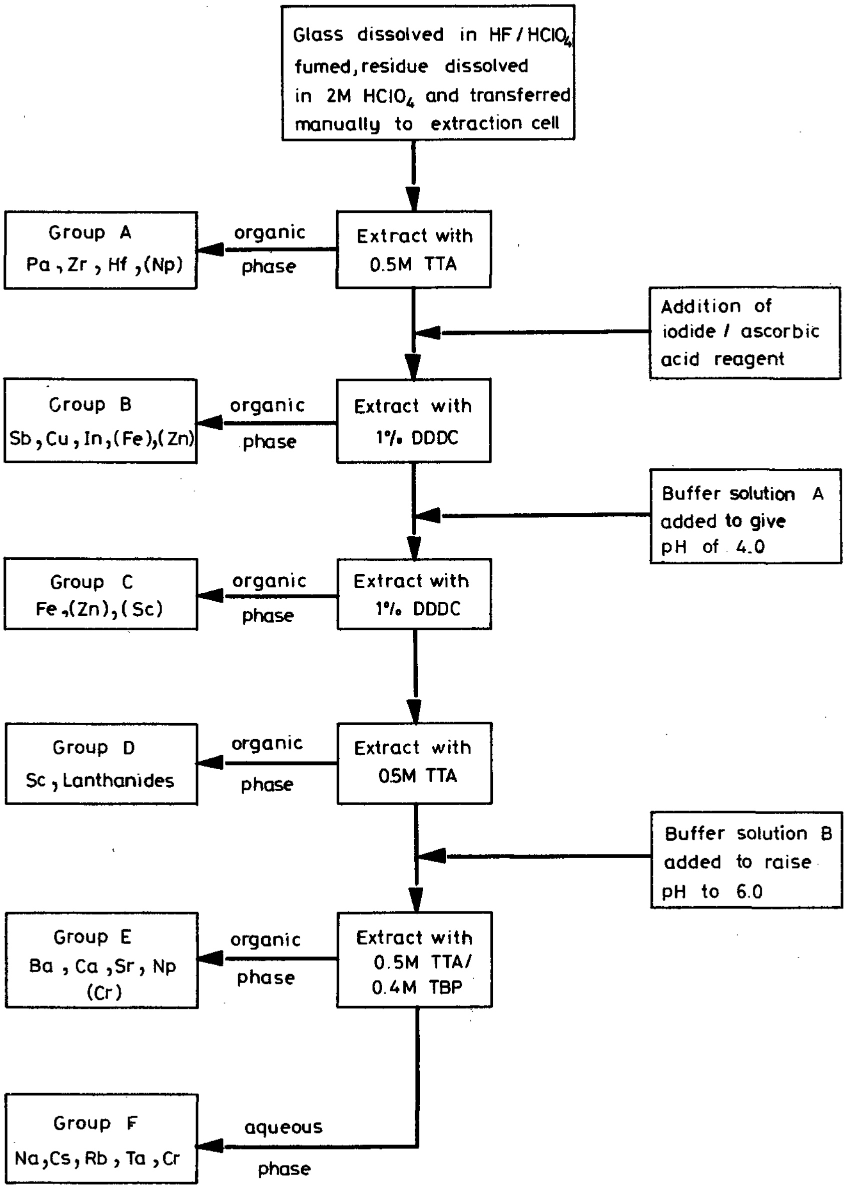

Fig. 3. Automated group separation scheme for analysis of glass

all the elements and for refractive index are shown in Figs 6-18. Using the χ^2 test it had been shown that the shape of these distributions is in each case significantly different from normal at the 0.05 probability level and only for elements As, Co, Sr and Yb can distributions be shown to be not significantly different from log normal at this level. It was therefore concluded that no simple general transformation of data into a Gaussian distribution was possible.

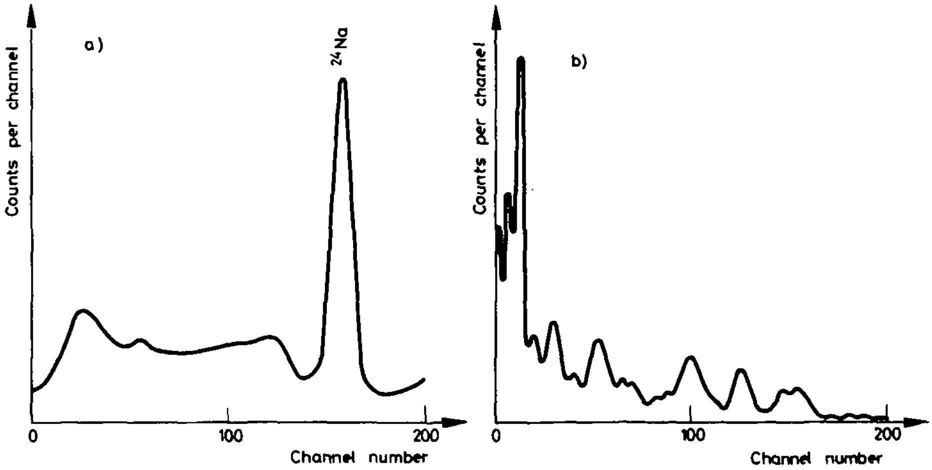

Fig. 4. Gross gamma-ray spectra for St. Helens glass. a - after 4-day decay, b - after 12-day decay

The present survey is the most extensive carried out in this country and it is believed that the distributions obtained are representative of the whole population. The almost complete lack of previous data for trace element concentrations makes comparison with other surveys impossible, however for refractive index a comparison with distributions from various scene-of-crime surveys can be made. It has been shown[5] that the refractive index distribution obtained for the 941 samples of the present survey is in fact significantly different statistically from those obtained on local scene-of-crime surveys, e.g. West Midlands survey 1968 by Cobb.[6] It is considered, however, that these differences can probably be attributed to the relatively small geographical area covered by such surveys and it is interesting to note that the closest agreement is obtained with a recent survey involving the collection of 150 glass samples from the whole of the Metropolitan area of London.[5]

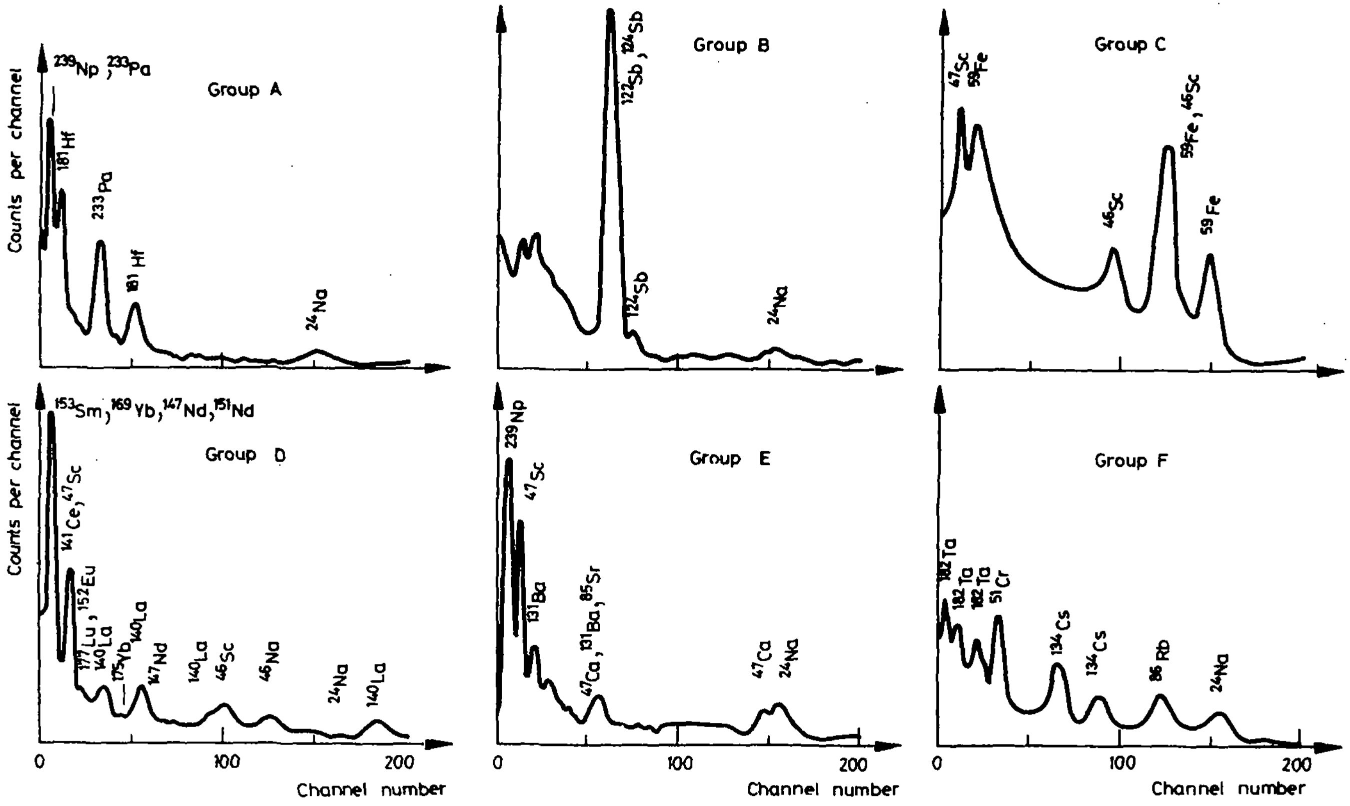

Fig. 5. Gamma-ray spectra for group extracts

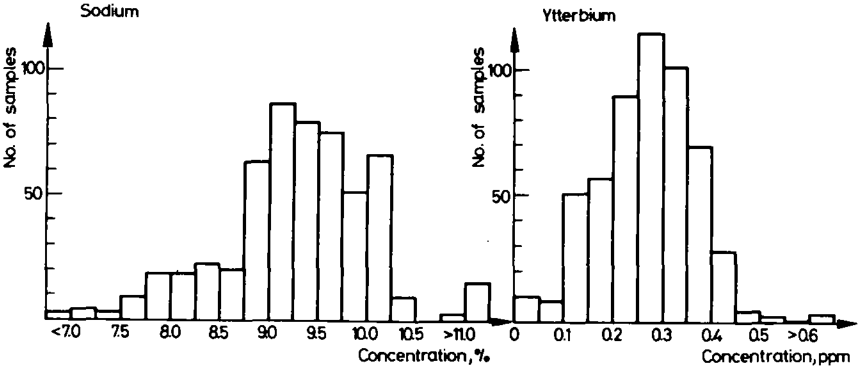

Fig. 6. Frequency distribution of sodium and ytterbium in glass

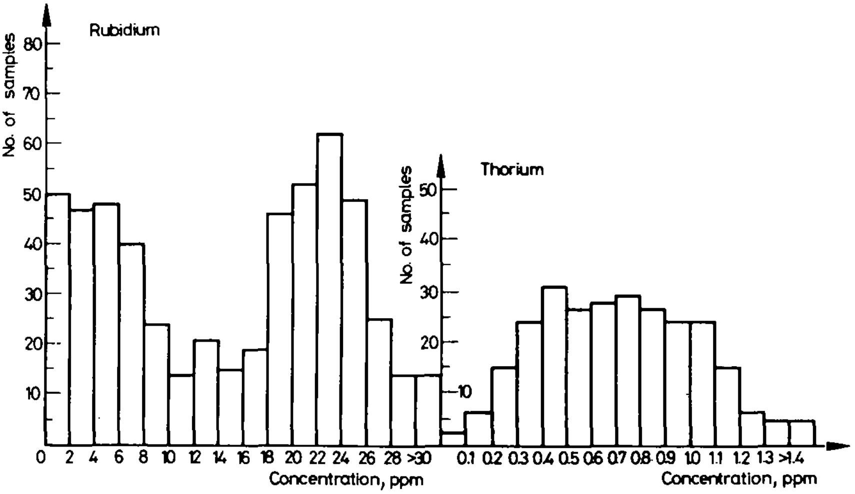

Fig. 7. Frequency distribution of rubidium and thorium in glass

The effect of building type

The glass samples collected in the survey were classified according to the type of building from which they were obtained, classification being: private dwellings, factory premises, shops, offices and other miscellaneous buildings. Table 1 shows the proportion of each type from the whole survey and from the 541 samples ana-

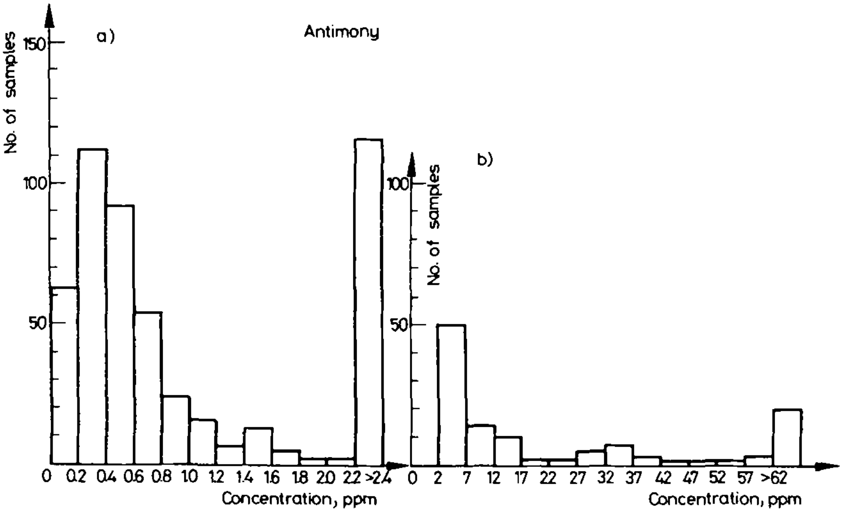

Fig. 8. Frequency distribution of antimony in glass. a - Modern glass distribution, b - other glass distribution

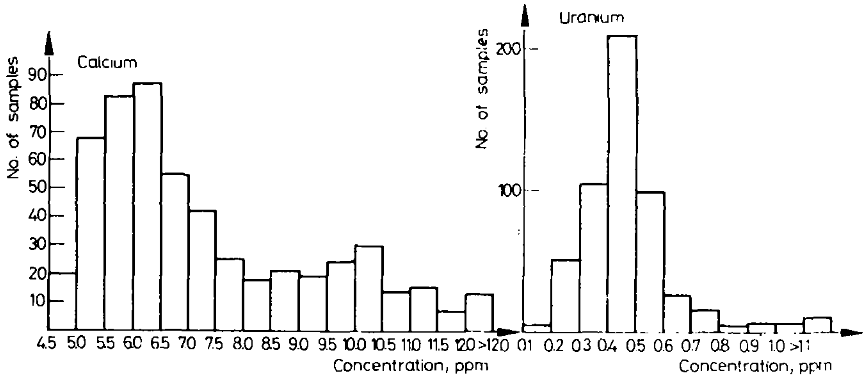

Fig. 9. Frequency distribution of calcium and uranium in glass

lysed by neutron activation. Using the χ^2 test it has been shown that there is no significant difference in the shape of the trace element distributions for different building types at the 0.05 probability level. Using refractive index data obtained using the Abbe refractometer for all survey samples Pearson and Dabbs[7] made a similar comparison using distributions for (a) private dwellings, (b) combined factories, shops and offices, and (c) other buildings and obtained the same result.

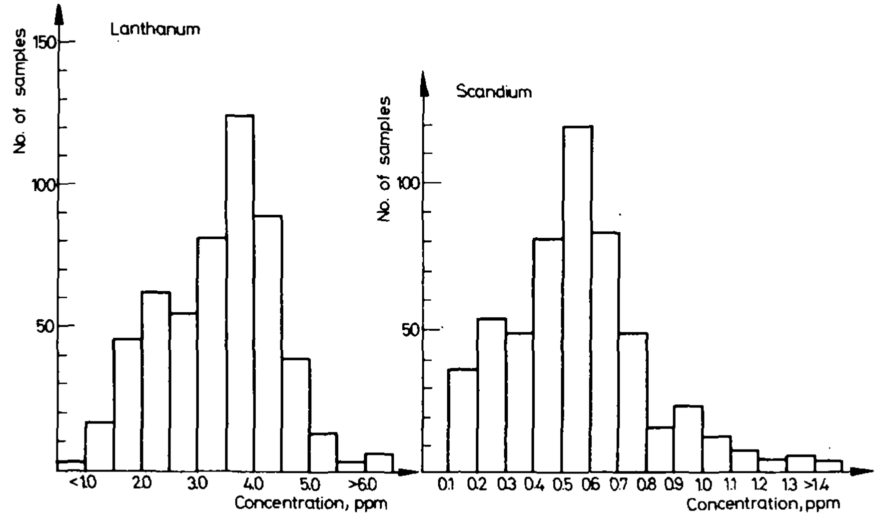

Fig. 10. Frequency distribution of lanthanum and scandium in glass

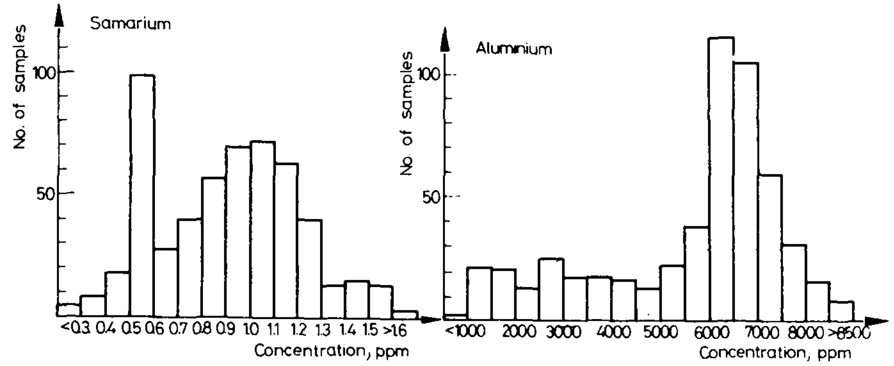

Fig. 11. Frequency distribution of samarium and aluminium in glass

The effect of geographical location

In addition to the original background data provided with survey samples a further regional classification has been introduced. Samples were classified geographically as follows:

Region 1 (South Eastern England) to include Bedfordshire, Berkshire, Essex, Hampshire, Hertfordshire, Kent, London, Middlesex, Oxfordshire, Surrey and Sussex.

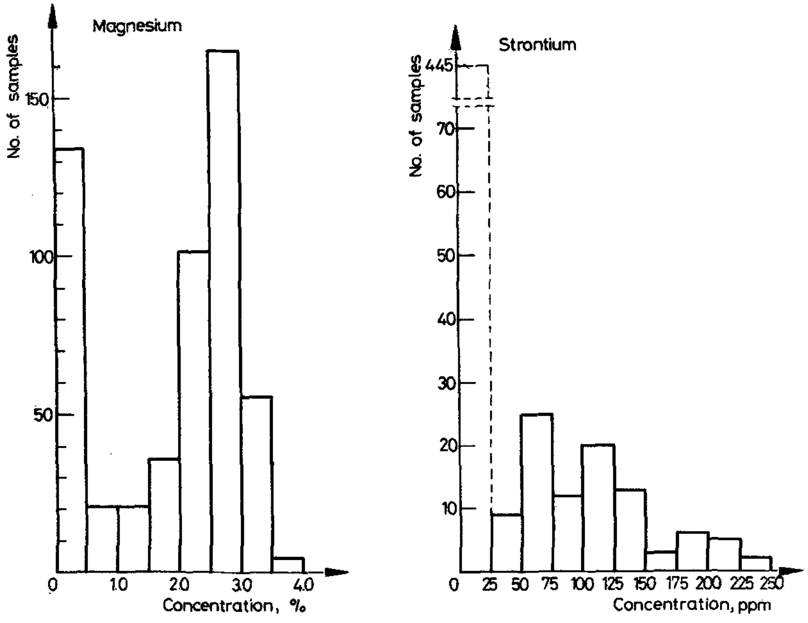

Fig. 12. Frequency distribution of magnesium and strontium in glass

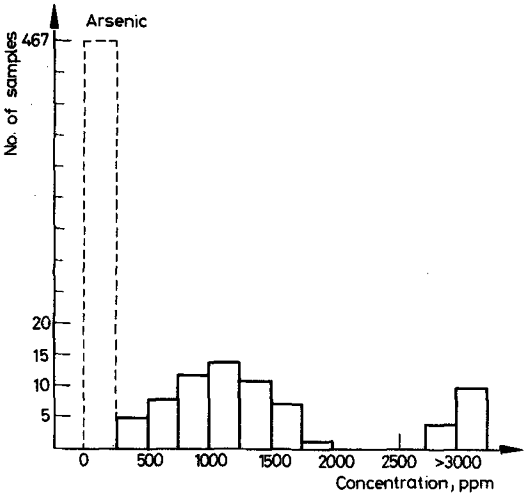

Fig. 13. Frequency distribution of arsenic in glass

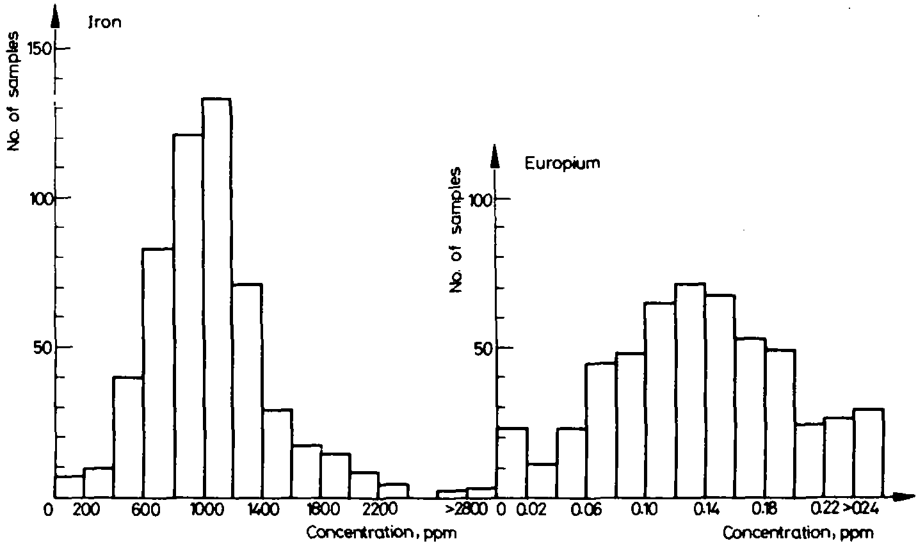

Fig. 14. Frequency distribution of iron and europium in glass

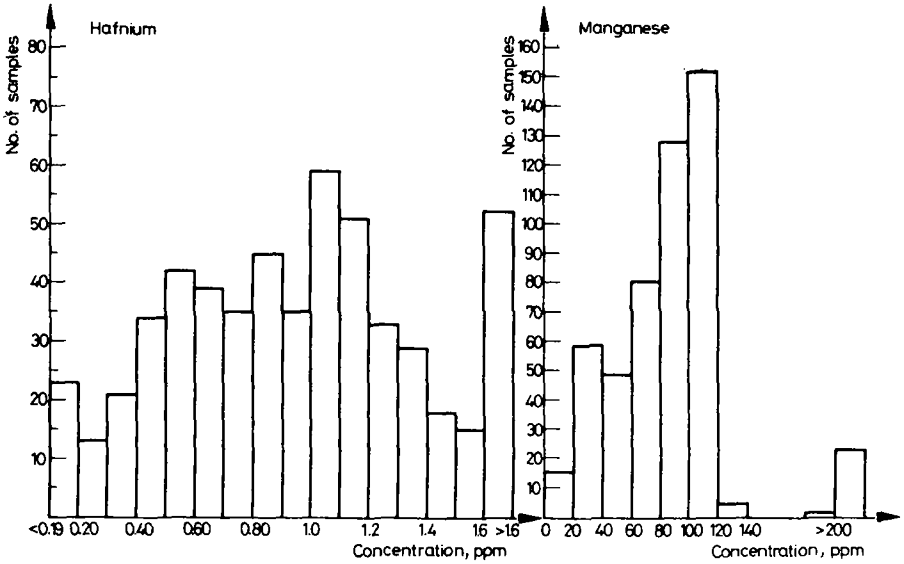

Fig. 15. Frequency distribution of hafnium and manganese in glass

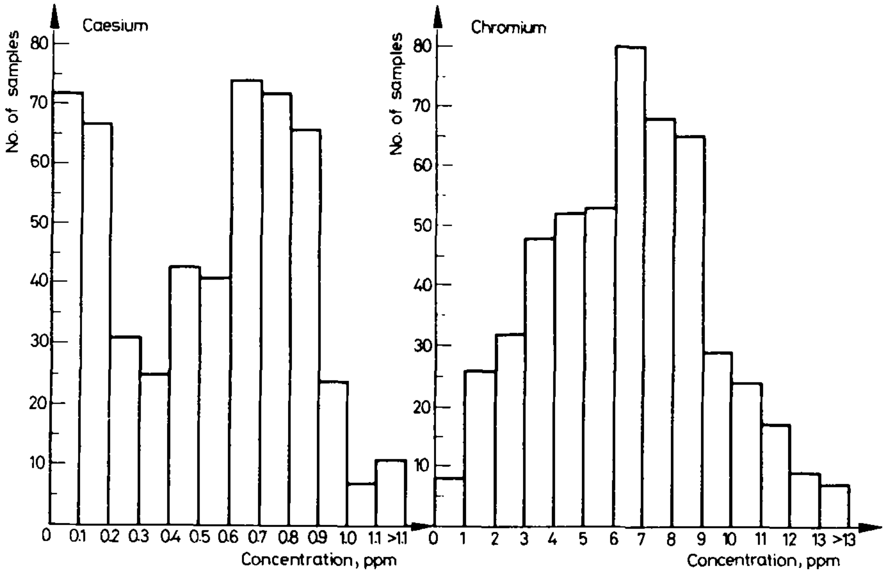

Fig. 16. Frequency distribution of caesium and chromium in glass

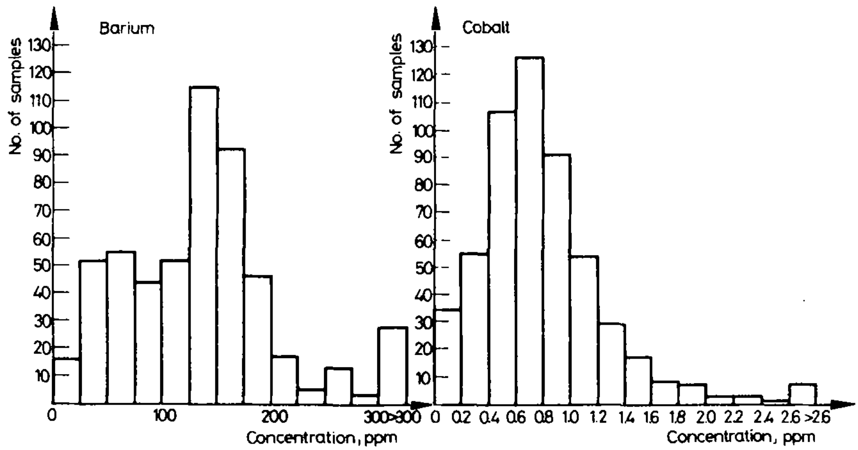

Fig. 17. Frequency distribution of barium and cobalt in glass

Region 2 (Midlands and Eastern England) to include Cambridgeshire, Cheshire, Derbyshire, Huntingdonshire, Leicestershire, Lincolnshire, Norfold, Northamptonshire, Nottinghamshire, Staffordshire, Suffolk, Warwickshire and Worcestershire.

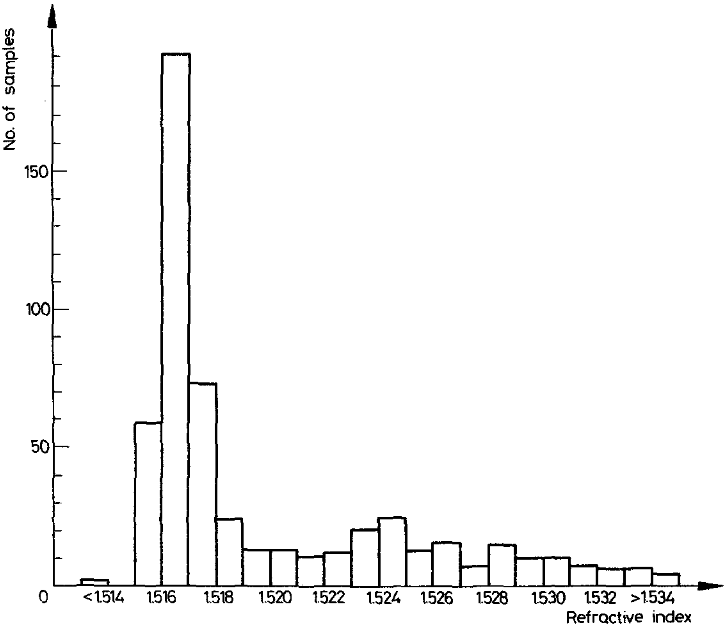

Fig. 18. Frequency distribution of refractive index for glass from scenes of fires

Region 3 (Wales and West England) to include Wales, Cornwall, Dorset, Devon, Gloucestershire, Herefordshire, Monmouthshire, Shropshire, Somerset and Wiltshire.

Region 4 (Northern England) to include Cumberland, Durham, Lancashire, Northumberland, Westmorland and Yorkshire.

Such a division was considered worthwhile since the production of modern flat glass is concentrated in a few major centres, widely spaced geographically, e.g. St. Hekens in Lancashire, Pontypool in Monmoutshire and Queenborough in Kent and this could well lead to significant regional variations in trace element distribution if manufacturers optimise the distribution of their products.

Previous work on multi-element analysis of glass[1,2] has shown that St. Helens glass can be readily distinguished from that manufactured at Pontypool or Queenborough, but differences between the latter two sites are relatively small. Taking the element rubidium as an indication of the source of the glass, being 20-30 ppm in glass from St. Helens compared to 0-10 ppm for glass from the other sites regional distributions for the concentration of this element are shown in Fig. 19. These differ significantly from each other and show a maximum contribution from St. Helens glass in the Northern regions, nearest to the site of manufacture to a minimum but significant contribution in Southern England and Wales. Similar observations have been made for a number of other elements including lanthanum, hafnium, and barium. These regional variations could be useful in future case work in providing a more accurate assessment of discrimination, however, at this stage statistical calculations have only been made using data for the whole survey. Statistically significant differences in the refractive index distributions for the regions (with the exception of region 1 compared to region 4) have also been observed.[5]

Table 1

Proportion of survey samples from various types of buildings

Type of building	Full survey, % (939 samples)	Multi-element survey, % (539 samples)
Private dwellings	49.0	47.5
Factory premises	16.2	16.1
Offices	2.1	2.4
Shops	10.2	8.9
Other buildings	22.5	25.0

Correlation of trace element concentrations

Strong correlations between a number of elements present in glass would be anticipated from the natural elemental correlations in the raw materials used in manufacture. The multi-element data for the 539 survey samples has been tested for correlation. The refractive index values are highly correlated with two major constituents, calcium ($r = 0.83$) and magnesium ($r = -0.71$), because there has been a gradual replacement of some calcium by magnesium which is known to lead to a corresponding change in physical properties. Other highly correlated elements have related chemical properties and therefore frequently occur together in natural materials. These include rubidium and caesium ($r = 0.84$) and the lanthanides, e.g. lanthanum-samarium ($r = 0.87$). Over half of the correlation coefficients are statistically significant and clearly need to be considered in statistical calculations for the discrimination of the multi-element method. Although Parker and Holford[8] have shown

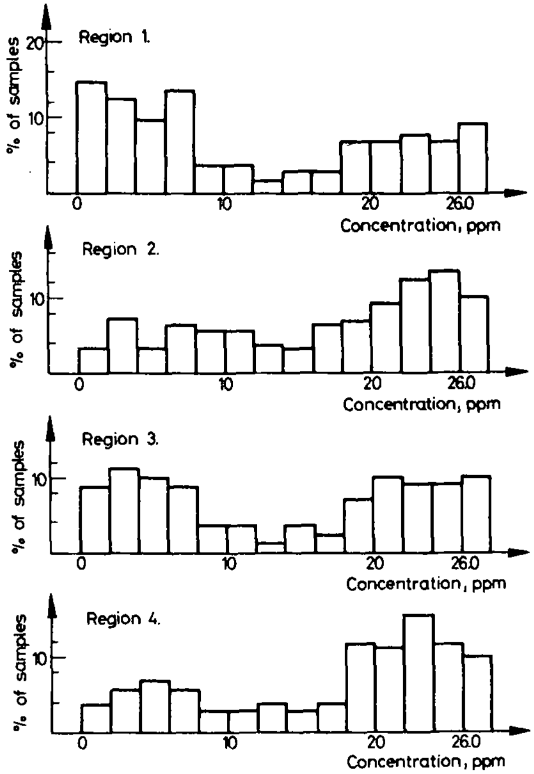

Fig. 19. Regional distributions of rubidium in glass

how to compare two objects with correlated attributes the computation is formidable for a large number of attributes. Therefore as an approximation which it is considered will not significantly affect the statistical calculations, eleven elements have been selected for which correlation coefficients are generally small and the data for these treated as uncorrelated. The elements used are: Al, As, Ba, Ca, Hf, Mn, Na, Rb, Sb, Sc, and Sr, the correlation coefficients of which are shown in Table 2.

Assessment of discrimination of the multi-element technique

The statistical method developed by Parker[2] for the general treatment of the identification problem has already been applied extensively on the comparison of human hair.[9] In a particular case the crime sample and controls are analysed and the reduced deviations in the concentration of each element are combined to produce a single criterion which indicates if the samples being compared are indistinguishable at a particular probability level. Further, if this test indicates the samples are similar then the proportion of the population (Q), in this case the fraction of the total amount of glass present throughout the whole country, which would appear similar to the sample can be calculated.

To give an overall assessment of the discrimination of the multi-element technique for glass proportion of the total glass population Q, similar to each of the 539 survey

Table 2

Elements selected for treatment as uncorrelated data

As	Ba	Ca	Hf	Mn	Na	Rb	Sb	Sc	Sr	Element
0.12	0.03	-0.21	0.02	-0.15	-0.29	0.65	-0.03	0.30	-0.02	Al
	0.10	-0.08	-0.24	0.57	-0.02	-0.07	0.29	0.04	0.68	As
		-0.04	-0.03	-0.01	0.05	0.01	-0.01	0.03	0,30	Ba
			0.03	-0.02	-0.34	-0.24	0.04	0.45	0.03	Ca
				-0.02	0.09	0.04	-0.01	0.15	-0.13	Hf
					0.07	-0.11	-0.01	0.01	-0.02	Mn
						-0.25	0.03	-0.45	-0.05	Na
							-0.11	0.37	-0.21	Rb
								-0.07	0.15	Sb
									0.19	Sc

samples has been determined. For these calculations, the eleven least correlated elements listed previously were used and mean and standard deviation values determined by replicate analysis of the major types of glass involved. A histogram showing the frequency values of Q ($\varepsilon = 0.01$) is given in Fig. 20b and cumulative data for Q shown in Table 3. Q values range from $9 \cdot 10^{-4}$ to $5 \cdot 10^{-12}$ with a median about $2.5 \cdot 10^{-6}$. These values should be used primarily as a means of comparing one technique with another on the same basis. This can be done with the refractive index data and Fig. 20a shows the Q-distribution so obtained from all survey samples assuming a value for λ_i of $4.0 \cdot 10^{-5}$ as determined by Dabbs and Pearson[4] using a Mettler hot-stage technique. This value was obtained by replicate determinations of refractive index and includes the variations over a pane of window glass. The large difference in discriminating power is well illustrated by comparison of the Q-distributions in Figure 20.

The absolute values of Q should not be used without some caution as they are from a survey based on a limited number of samples. For the most common samples the Q-values are of the right magnitude, as the calculation of Q gives values of the order of 10^{-3} and direct comparison of individual glasses indicates that only 2 pairs were indistinguishable out of 539 samples. For the rarest samples, $Q < 10^{-11}$ then it implies that it is possible to distinguish a glass of a few grams weight from all other

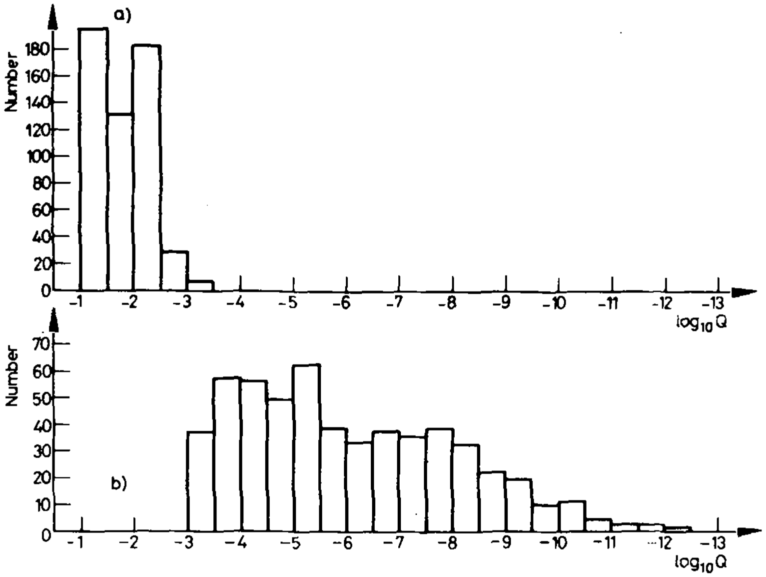

Fig. 20. Distribution of Q values. a - Refractive index, b - multielement analysis

window glass in the country. This is unlikely to be true and arises from the assumption that the frequency distributions are smooth. In practice it is probable that the true distributions are not smooth if examined in fine detail, particularly towards the extremes of the distributions. Each batch produced will consist of several tons of glass of virtually similar composition whilst at certain specific concentrations there will be very few samples as this does not coincide with the concentration range of a particular batch of glass.

If such a method of assessing discrimination is used in particular cases and Q-values of greater than, say, 10^{-6} are obtained in practice this means that this particular glass is rare but too much reliance should not be placed on the Q-value itself.

Simulated case studies

To illustrate how multi-element analysis might be applied to practical forensic science problems three simulated cases have been studied, For these three different types of glass (St. Helenes, Pontypool and Belgian) were selected as controls. In each case eight control samples were first analysed to determine the mean concentration and standard deviation for the eleven elements of interest. Using the non-destructive method involving a one minute irradiation eight separate 1 mg samples of glass were used, results being obtained for Al, As, Mn, and Na. For the application of the long irradiation technique followed by radiochemical separation each group of eight control samples were irradiated simultaneously to minimise errors due to neutron flux variations and results for Ba, Ca, Hf, Rb, Sc, and Sr obtained.

Table 3
Cumulative data for Q for glass survey

Q value	Cumulative $\% \leq Q$
$9.0 \cdot 10^{-4}$	100
$2.3 \cdot 10^{-4}$	90
$7.0 \cdot 10^{-5}$	80
$2.3 \cdot 10^{-5}$	70
$6.0 \cdot 10^{-6}$	60
$2.5 \cdot 10^{-6}$	50
$5.0 \cdot 10^{-7}$	40
$8.0 \cdot 10^{-8}$	30
$1.2 \cdot 10^{-8}$	20
$1.2 \cdot 10^{-9}$	10
$2.1 \cdot 10^{-10}$	5
$2.9 \cdot 10^{-11}$	2
$9.0 \cdot 10^{-12}$	1

Three separate cases were then simulated by mixing one piece of each of the three control samples with a further seven pieces of glass randomly selected from the survey. All samples were then analysed by the two neutron activation techniques giving data for the concentrations of eleven elements. The combined deviations C of each of these eight samples from the mean of the appropriate controls were calculated. The results are shown in two groups in Table 4.

The data presented in Table 4a was calculated from results for the four elements (Al, As, Mn and Na) obtained using the non-destructive short irradiation procedure. It can be seen that from this relatively limited data the method correctly identifies samples 1 as indistinguishable from the control sample in each case but for case A involving the St. Helens control a further sample (sample 3) is also found indistinguishable setting the C_0 criterion at 0.01.

Using the additional data provided by the long irradiation method (Table 4b) the discrimination is increased such that correct identification of sample 1 only occurs in each case. The value of Q, viz. the fraction of the total glass population which would appear similar to the control samples, is also calculated and shown in Table 4b. The values of Q obtained range from 5.8 · 10^{-6} for the St. Helens control to 2.8 · 10^{-8} for the Belgian glass and indicate the extremely high discrimination which can be achieved by the multi-element technique.

Table 4

Simulated case studies

(a) Using data from short irradiations only

Case / Unknown glass glass	Combined deviations C (C_0 = 13.3)							
	1	2	3	4	5	6	7	8
A (St. Helens)	11.0	764	12.7	37.4	2956	54.0	1190	8422
B (Pontypool)	0.80	908	262	53.3	109	61.3	405	1176
C (Belgian)	1.78	380	453	213	288	512	483	403

(b) Using data for eleven elements

Case / Unknown glass	Combined deviations C (C_0 = 24.7)								Q
	1	2	3	4	5	6	7	8	
A (St. Helens)	19.3	1903	74.2	112	26992	145	5781	11976	$5.79 \cdot 10^{-6}$
B (Pontypool)	8.4	4244	5353	173	828	2062	9043	4164	$1.35 \cdot 10^{-8}$
C (Belgian)	3.9	884	1302	304	469	776	10911	1177	$2.77 \cdot 10^{-8}$

In each case sample 1 of the "unknown glass" is the sample identical to the controls.

Conclusions

This study indicates that multi-element analysis is a discrimination method of comparing glass fragments. The method of analysis involving a radiochemical separation may not be suitable for all types of case samples. The application of non-destructive methods relying on sodium iodide and germanium gamma-spectrometers for the measurement of induced activity will also be discussed.

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This report makes use of earlier work on glass which was supported by the Home Office on a contract basis.

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