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Application of internal monostandard neutron activation analysis method in elemental analysis of car glasses for forensic study

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Abstract: The use of nuclear techniques for elemental analysis has been successfully developed in many laboratories in the IAEA Member States, including Vietnam. Nuclear techniques have also been proven to be extremely powerful in provenancing samples relevant to forensics. In the framework of the CRP project on Enhancing Nuclear Analytical Techniques to Meet the Needs of Forensic Sciences (IAEA CRP F11021), a total of 19 elemental concentrations in 48 car glass samples has been determined by the internal monostandard neutron activation analysis (IM-NAA) method. In this work, obtained results from the statistical analysis indicated that rare earth elements (La, Ce, Sm, Eu, Tb, Yb), transition elements (Sc, Mn, Fe, Co, Zn, Hf, Cs, Ba, Rb), and major elements (Al, Na, Fe, Ca) play a significant role in the group study of car glasses.

Keywords: *INAA, car glasses, REEs, forensic science.*

I. INTRODUCTION

The nuclear analysis techniques play important roles in provenancing samples relevant to the forensic study. The possible areas of forensics applications include, but are not limited to, crime investigation, food safety and health-related issues, cultural heritage artifacts and environmental samples. Although analytical techniques related to the above areas are readily available and routinely applied in research, there is still a considerable gap when it comes to routine forensics applications. The development of these techniques as a recognized application for forensics requires awareness building, coordinated support and, in some cases, accreditation of the involved laboratories. Furthermore, promotion of the capabilities and establishing closer links among the end-users, service providers and other stakeholders in this particular area still needs to be enhanced and better organized. The IAEA assists Member States by providing technical assistance on the conduct of a nuclear forensics examination, training, coordinated research programmes as well as nuclear forensic advisories and consultations. In the period 2017-2021, the CRP project on Enhancing Nuclear Analytical Techniques to Meet the Needs of Forensic Sciences (IAEA CRP F11021) has been performed [1]. The project aims to develop and utilize the unique capabilities of nuclear analytical techniques towards recognized needs of forensic sciences and to contribute to capacity building and long-term collaboration and networking between the practitioners of nuclear analytical techniques and forensic science stakeholder communities resulting in demonstrable societal gains and enhanced public recognition.

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The neutron activation analysis (NAA) laboratory of the Dalat Nuclear Research Institute has participated in the research contract to improve the applicability of the NAA technique for forensic study. Samples requested by the IAEA include car glass and silver coin samples. In the present work, the analysis of chemical compositions of car glasses by the NAA technique combined with multivariate statistical methods allowed to provide information related to classification, grouping and identification of car glass characteristics. Based on the results of analysis compositions obtained from member countries, the IAEA establishes a database of car glasses worldwide for further forensic investigation.

II. EXPERIMENTAL

A. Sample preparation, irradiation and measurements

Forty-eight car glass fragment samples with different forms were weighed and packed in polyethylene bags. The samples were grouped as follows:

- By manufacturer: Mazda, Peugeot, Hyundai, Honda, Ford, Daewoo, Fiat, Mitsubishi, Surabu, Renault.

- By model: Latis, 206, Accent, Civic, Focus, Lanos, Punto, Pajero, Impreza, Clio.

- By position: Left, Right, Front Back, Back triangle.

A photograph of car glass samples is shown in Fig. 1.

Fig. 1. Car glass samples for NAA

The samples were irradiated at channel 7-1 and rotary specimen rack of the Dalat research reactor (DRR) for short-lived and long-lived radioactive nuclides, respectively. The experimental parameters are described in Table 1. After an appropriate decay time, the irradiated samples were then counted on a gamma spectrometer using an HPGe detector with 30% relative efficiency and 2.1 keV resolution at 1332.5 keV of ^{60}Co. The distance between the sample and detector can be varied from 10 to 15 cm to keep the dead time less than 10% and eliminate true coincidence effects.

B. Data processing

The k0-based internal monostandard method in neutron activation analysis (IM-NAA) has been applied to analyse elemental concentrations of irregularly shaped samples, in this case fragment car glasses [2]. In IM-NAA, the mass ratio of element x to y can be expressed as follows [3]:

$$\frac{m_x}{m_y} = \frac{(S.D.C)_y \left[f + Q_0(\alpha) \right]_y}{(S.D.C)_x \left[f + Q_0(\alpha) \right]_x} \frac{P_{E_x}}{P_{E_y}} \frac{\varepsilon_{E_y}}{\varepsilon_{E_x}} \frac{k_{0,E_y}}{k_{0,E_x}} \quad (1)$$

Where $Q_0(\alpha)$ is the ratio of the resonance integral-to-thermal neutron cross-section corrected for the non-ideal epithermal neutron flux distribution α, and is calculated as:

$$Q_0(\alpha) = \frac{I_0(\alpha)}{\sigma_0} = \frac{Q_0 - 0.429}{\bar{E}_r^{\alpha}} + \frac{0.429}{E_{Cd}^{\alpha}(2\alpha + 1)} \quad (2)$$

Where subscripts x and y refer to the analyte elements and internal standard element (Sc). $Q_0 = \frac{I_0}{\sigma_0}$ is the resonance integral 1/E to 2200 m.s^{-1} cross-section ratio; P_E is the net area of the gamma peak; $S = 1 - e^{-\lambda t_i}$, $D = e^{-\lambda t_d}$, $C = \frac{1 - e^{-\lambda t_c}}{\lambda t_c}$ are saturation, decay and measurement factors where t_i, t_d, t_c are irradiation, decay and counting times, respectively; $\bar{E}_r$ is the effective resonance energy; E_{Cd} is the effective cadmium cut-off energy; f is the thermal to epithermal neutron flux ratio; ε_E is the relative efficiency and $k_{0,E}$ is the k_0 factor [3, 4].

Due to different shape of the glass samples, the relative detection efficiency is determined by using gamma rays emitted from the decay of the nuclei in the activated sample such as ^{59}Fe (142, 192, 1099, 1291 keV), ^{134}Cs (563, 569, 604, 796, 801, 1365 keV), ^{152}Eu (121, 244, 444, 778, 1085, 1112, 1408 keV), and ^{160}Tb (299, 879, 1178, 1272, 1312 keV). The relative detection efficiency in the energy range of 121 ÷ 1408 keV has been determined and it is shown in Fig. 2.

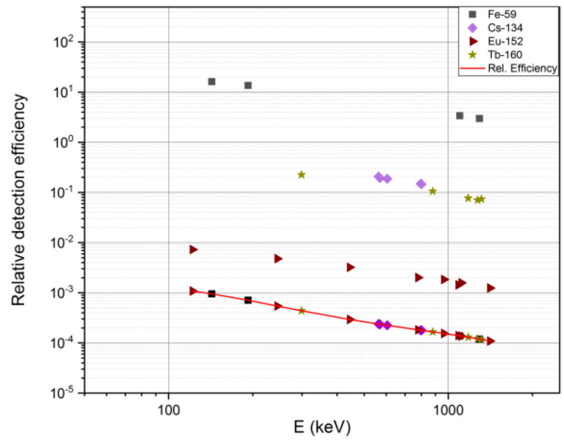

Fig. 2. A typical relative detection efficiency plot of an activated sample

An in-house software called IM-NAA has been used to calculate relative detection efficiencies and elemental concentrations using the IM-NAA method [2]. After the relative efficiency calibration curve was constructed, relative concentrations can be calculated from Eq. (1).

In this study, the XLSTAT program was used for statistical analysis [5]. The data of elemental concentrations in the 48 samples were normalized on a scale of 0-1 because of the large difference in concentrations between the major elements and trace elements (rare earth elements). The normalization reduced the influence of these gaps in the dataset. The following statistical methods as Descriptive statistics, Correlation tests and Agglomerative Hierarchical Clustering were used for data analysis in this study.

Table I. Irradiation, decay and counting times for car glass samples

Irradiation position (Neutron flux (n.cm^{-2}.s^{-1}), f, α)	Irradiation time	Decay time	Counting time	Nuclides
Channel 7-1 (4.22 x 10^{12}, 9.7, -0.031)	60 sec	10-15 min	120 sec	^{28}Al
		1-2 hrs	600 sec	^{56}Mn, ^{49}Ca
Rotary Rack (3.61 x 10^{12}, 35.7, 0.073)	10 hrs	2-3 days	1800 sec	^{24}Na, ^{131}Ba, ^{140}La, ^{153}Sm
		20-30 days	10800 sec	^{141}Ce, ^{60}Co, ^{134}Cs, ^{152}Eu, ^{59}Fe, ^{181}Hf, ^{86}Rb, ^{233}Pa(Th), ^{46}Sc, ^{160}Tb, ^{169}Yb, ^{65}Zn

Table II. Descriptive statistics of elemental concentrations

Statistic	No. of observations	Minimum (mg/kg)	Maximum (mg/kg)	Mean (mg/kg)	Standard deviation (n-1)	RSD (%)
Al	48	6799	18000	11788	2597	22.03%
Ca	48	31930	71230	51830	7893	15.23%
Mn	48	12	176	60	35	58.77%
Na	48	10040	125300	103487	19097	18.45%
La	48	1.45	11.80	4.44	2.15	48.41%
Sm	48	0.18	2.32	0.61	0.38	61.85%
Sc	48	0.11	2.99	0.55	0.53	95.54%
Fe	48	2053	8009	4313	1407	32.63%
Co	48	0.19	14.00	4.82	4.37	90.70%
Zn	48	1.00	10.80	4.49	2.57	57.17%
Rb	48	1.00	30.00	12.39	7.83	63.21%
Cs	48	0.01	0.77	0.29	0.20	68.93%
Ba	48	6.9	115.0	63.0	30.1	47.74%
Ce	48	1.0	160.0	16.1	28.0	173.65%
Eu	48	0.03	0.51	0.12	0.08	67.30%
Tb	48	0.02	0.33	0.09	0.07	77.58%
Yb	48	0.06	1.21	0.31	0.22	70.62%
Hf	48	0.44	4.33	1.47	0.91	61.88%
Th	48	0.27	3.36	1.57	0.99	63.06%

III. RESULTS AND DISCUSSION

Nineteen elements, namely Al, Ca, Mn, Na, La, Sm, Sc, Fe, Co, Zn, Rb, Cs, Ba, Ce, Eu, Tb, Yb, Hf, and Th were quantified in 48 car glass samples with different sizes and shapes by IM-NAA method whereas Sc was chosen for an internal standard. In Table II, descriptive statistics describe information of the dataset including min, max, mean, and standard deviation of elemental concentrations.

The analysis results in Table II show that rare earth elements (REEs) and some other elements have a high standard deviation (RSD> 45%). We already knew the natural correlation between elements in the same group. Examples of correlations between elements in groups are: (1) Large ion lithophile group includes: Cs, Rb, Ba with the addition of divalent Eu. These elements feature large ionic radii, low electrical charge (valence 1, rarely 2) and are the most mobile in various chemical processes; (2) Group of strong force field elements (HFS-High Field Strength). The immobile elements are Sc, Th, Hf and REEs: La, Ce, Sm, Eu, Tb, Yb. Strong force field elements are less mobile, especially in different geological processes; (3) The group of transition elements includes Sc, Mn, Fe, Co, Zn. In geological processes, transition elements are more dynamic than strong field elements. The correlation between the elements in the glass sample group is presented in Table III.

The correlation can be classified according to the correlation coefficient r as follows: (1) $r<0.3$ very weak correlation; (2) $0.3\leq r < 0.6$ moderate correlation; (3) $r \geq 0.6$ strong correlation. The results in Table 3 show the strong correlation of elements among the REEs group which can be used as indicators to identify or classify these samples.

Table III. Correlation between elements in glass sample group (Pearson method)

Ele.	Al	Ca	Mn	Na	La	Sm	Sc	Fe	Co	Zn	Rb	Cs	Ba	Ce	Eu	Tb	Yb	Hf	Th
Al	1.00	0.57	0.37	-0.34	0.31	0.17	0.15	-0.19	0.47	0.36	0.44	0.36	0.28	0.08	0.18	0.06	0.26	0.34	0.21
Ca	0.57	1.00	0.04	0.02	0.27	0.10	0.10	-0.19	0.47	0.18	0.14	0.14	-0.01	-0.04	0.18	0.12	0.22	0.20	0.34
Mn	0.37	0.04	1.00	-0.31	0.10	0.02	0.01	-0.03	0.19	0.07	0.11	-0.05	0.06	-0.06	0.00	0.11	0.01	0.07	0.04
Na	-0.34	0.02	-0.31	1.00	0.01	-0.02	-0.03	0.18	-0.18	-0.16	-0.03	-0.09	0.05	0.21	-0.01	0.10	-0.12	0.21	0.28
La	0.31	0.27	0.10	0.01	1.00	0.84	0.74	-0.17	0.31	0.30	0.08	0.03	0.12	0.13	0.82	0.62	0.69	0.47	0.75
Sm	0.17	0.10	0.02	-0.02	0.84	1.00	0.89	0.05	0.02	0.28	-0.07	-0.06	-0.04	0.00	0.94	0.72	0.80	0.28	0.63
Sc	0.15	0.10	0.01	-0.03	0.74	0.89	1.00	-0.16	0.10	0.18	0.01	-0.11	-0.11	0.07	0.96	0.65	0.89	0.33	0.46
Fe	-0.19	-0.19	-0.03	0.18	-0.17	0.05	-0.16	1.00	-0.66	0.10	-0.38	-0.14	0.08	-0.09	-0.12	-0.13	-0.13	-0.09	-0.15
Co	0.47	0.47	0.19	-0.18	0.31	0.02	0.10	-0.66	1.00	0.17	0.43	0.24	0.20	-0.19	0.14	0.06	0.16	0.39	0.37
Zn	0.36	0.18	0.07	-0.16	0.30	0.28	0.18	0.10	0.17	1.00	-0.01	0.01	0.37	-0.20	0.22	0.11	0.18	0.25	0.18
Rb	0.44	0.14	0.11	-0.03	0.08	-0.07	0.01	-0.38	0.43	-0.01	1.00	0.84	0.41	0.56	-0.01	-0.05	0.06	0.09	0.14
Cs	0.36	0.14	-0.05	-0.09	0.03	-0.06	-0.11	-0.14	0.24	0.01	0.84	1.00	0.35	0.54	-0.09	-0.11	-0.04	-0.11	0.06
Ba	0.28	-0.01	0.06	0.05	0.12	-0.04	-0.11	0.08	0.20	0.37	0.41	0.35	1.00	0.25	-0.09	-0.06	0.00	0.29	0.09
Ce	0.08	-0.04	-0.06	0.21	0.13	0.00	0.07	-0.09	-0.19	-0.20	0.56	0.54	0.25	1.00	0.02	0.00	0.07	-0.13	-0.06
Eu	0.18	0.18	0.00	-0.01	0.82	0.94	0.96	-0.12	0.14	0.22	-0.01	-0.09	-0.09	0.02	1.00	0.69	0.86	0.32	0.61
Tb	0.06	0.12	0.11	0.10	0.62	0.72	0.65	-0.13	0.06	0.11	-0.05	-0.11	-0.06	0.00	0.69	1.00	0.51	0.23	0.61
Yb	0.26	0.22	0.01	-0.12	0.69	0.80	0.89	-0.13	0.16	0.18	0.06	-0.04	0.00	0.07	0.86	0.51	1.00	0.43	0.36
Hf	0.34	0.20	0.07	0.21	0.47	0.28	0.33	-0.09	0.39	0.25	0.09	-0.11	0.29	-0.13	0.32	0.23	0.43	1.00	0.46
Th	0.21	0.34	0.04	0.28	0.75	0.63	0.46	-0.15	0.37	0.18	0.14	0.06	0.09	-0.06	0.61	0.61	0.36	0.46	1.00

Fig. 4 shows the result of Agglomerative Hierarchical Clustering (AHC). AHC was based on the differences in Euclidean distance between the objects to be grouped. One of the outputs is a dendrogram, which illustrates the progressive clustering of data. It is thus simple to determine the appropriate number of classes from the dendrogram. In Fig. 4, the car glasses can be divided into 3 large groups. The first group includes Fiat, Ford, Peugeot, Renault and Honda. The second group includes Mazda and Surabu and the third group includes Daewoo, Hyundai, and Mitsubishi.

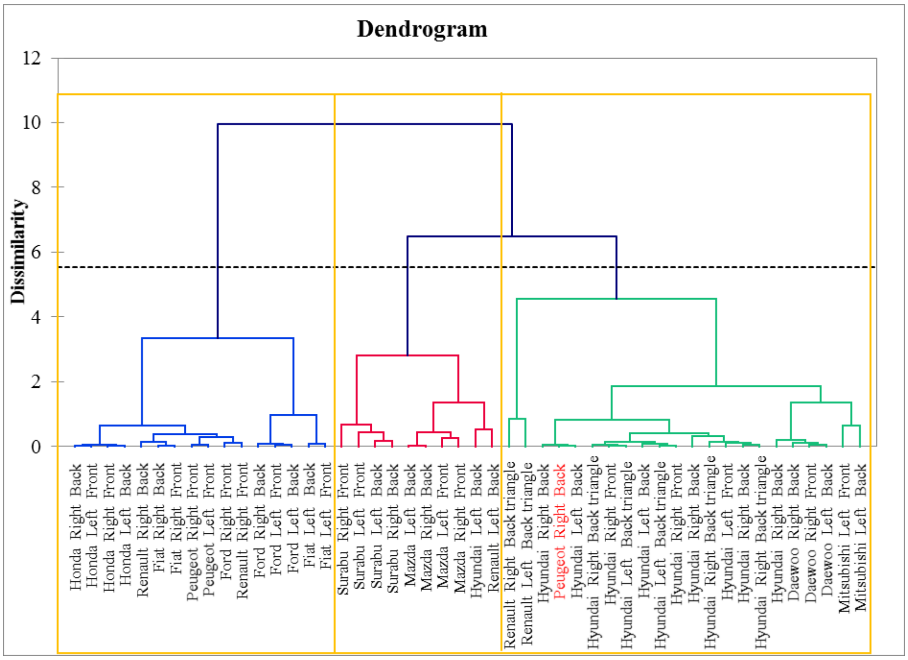

Fig. 4. Dendrogram by car manufacturers

For the first group, car manufacturers are mainly American and European brands, except Honda (Japan). The information provided by the IAEA also suggests that there is a high probability that Honda car glasses may be manufactured in Europe. The second largest group belongs to two Japanese car manufacturers: Mazda and Surabu. This group is also divided into two subgroups belonging to two separate brands. The third largest group belongs to Korean car manufacturers including Hyundai and Daewoo. In addition, the Japanese Mitsubishi is also classified in this group, but it is quite separate from the Korean car group. Similarly, two Renault triangular car glasses are classified in this group but they are distributed separately. These samples can be made with special materials that are not included in the identified groups and are also different from the Renault glasses distributed in the first group. The rear right glass of Peugeot is a special case that should be in the first group with other Peugeot glasses, but after classification, this glass is in the Korean car group. It can be explained this glass is replaced by Korean car manufacturers.

To have more information on elements correlation, the data set was analysed by principal component analysis (PCA). This method was used to investigate the car glass data. The purpose was to explore the relationships between the elements. The PCA plot of elements were shown in Fig. 5. The principal component loadings are also called the correlation circle. When two variables are far from the center, they are significantly positively correlated if they are close to each other (correlation coefficient close to 1); orthogonal (correlation coefficient close to 0); and significantly negatively correlated if they are on opposite sides of the center (correlation coefficient close to -1). Fig. 5 shows that the REEs and Th are strongly correlated with each other, and principal component 1 (F1) is presented the largest variance of the data set (39.13%). In the case of identification, classification and grouping, the REEs have more advantages and can be the indicator elements that identify or classify these samples.

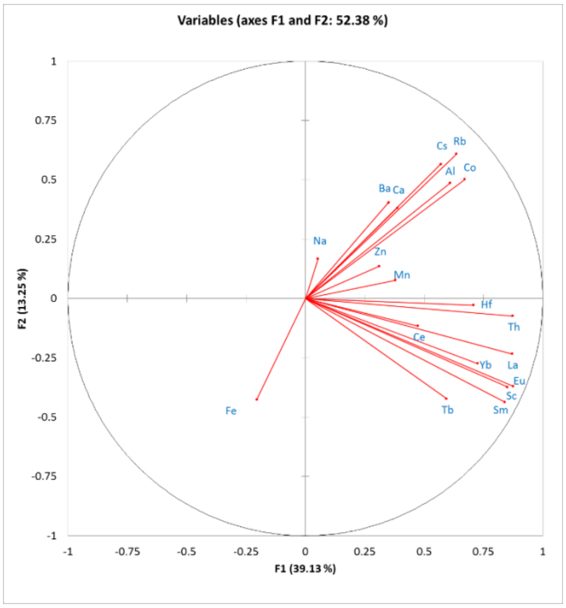

Fig. 5. PCA plot of elements in car glass

IV. CONCLUSIONS

The analytical results of elemental concentrations using the IM-NAA associated with multivariate statistical methods have provided information on the relationship between the different manufacturers of car window glass through chemical composition. REEs are the specific source and key marker elements and can be used to group samples to identify them belonging to the same or different sources. The present work contributes to capacity building and long-term collaboration and networking between the practitioners of nuclear analytical techniques and forensic science stakeholder communities resulting in demonstrable societal gains and enhanced public recognition. Further, the IM-NAA associated with multivariate statistical methods can be applied to pottery and bread provenance in archaeology studies.

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