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Measurement of effective atomic number of gunshot residues using scattering of gamma rays

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HIGHLIGHTS

- Values of Z_{eff} depend on the chemical content of the investigated gunshot residues.
- The agreement of measured values of effective atomic numbers with theoretical calculations is quite satisfactory.
- The present calculations of Z_{eff} have thrown new light on forensic science.

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ABSTRACT

Better understanding of gunshot residues and the major elemental composition would be valuable to forensic scientists for their analysis work and interpretation of results. In the present work, the effective atomic numbers of gunshot residues (cartridge case, bullet core, bullet jacket and gunpowder) were analyzed using energy dispersive X-ray analysis (EDX). The scattering of 59.54 keV gamma rays is studied using a high-resolution HPGe detector. The experiment is performed on various elements with atomic number in the $4 \leq Z \leq 82$. The intensity ratio of coherent to Compton scattered peaks, corrected for photo-peak efficiency of gamma detector and absorption of photons in the sample and air, is plotted as a function of atomic number and constituted a best-fit-curve. From this fit-curve, the respective effective atomic numbers of gunshot residues are determined.

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1. Introduction

When a gun is fired, in addition to the bullet, many other materials exit the barrel of the weapon, and are collectively termed gunshot residue (GSR). GSR is mainly composed of gunpowder, ignition primer and metals. The latter arise from the cartridge case, bullet, bullet coating and metal jacket often containing brass or lead, sometimes with nickel coating, and lead or antimony from the bullet core.

Gunshot residues can be detected and identified by various analytical methods such as flame-less atomic absorption spectroscopy (FAAS) (Renshaw et al., 1973), neutron activation analysis (NAA) (Menke et al., 1973; Lukens et al., 1970), emission spectral analysis (ESA) (Miklyeva and Stepanova, 2003), polarography (Vaněrková et al., 2002), optical microscopy, qualitative chemical tests, diffusion chromatography and inductively coupled plasma atomic emission spectrometry (ICP-AES) (Koons et al., 1988). There are a number of

reports available about the detection of gunshot residues by the SEM-EDX method (Dimaio et al., 1987; Goldstein et al., 1984; Gunaratnam and Himberg, 1994; Kazimirov et al., 2006; Waghmare et al., 2004). The SEM-EDX technique can be used to study the exhibit materials such as gunshot residue (GSR) particles, providing both their characteristic image and an energy dispersive X-ray spectrum.

X-ray fluorescence analysis is mainly used to investigate the elemental composition of gunshot residues, to determine the combination of elements in the test specimen that are characteristic of gunshot residues, to determine the distance and direction of the shot and to establish the hand in which the gun was held at the time the shot was fired. X-ray fluorescence analysis has some advantages: X-ray fluorescence analysis is faster, less error prone, needs uncomplicated sample preparation and is nondestructive. Also, the X-ray fluorescence analysis method seems promising to study the composition of gunshot residues (Meng and Chen, 2006).

An effective atomic number provides conclusive information about the complex medium (Hine, 1952). There exist a number of experimental techniques, which are used to determine effective

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atomic number and electron density, like chemical analysis, atomic absorption spectroscopy, particle-induced X-ray emission (PIXE), X-ray fluorescence (XRF), proton-induced gamma ray emission (PIGE), fast neutron activation analysis (FNAA), acoustic methods and the electrical impedance method (Singh et al., 2007). X-ray scattering techniques are non-destructive and often have a great advantage over the traditional chemical techniques used for determination of the effective atomic number of unknown samples. X-ray scattering is the energy dispersive X-ray analysis (EDX). But, the X-ray scattering method uses coherent and Compton peaks. X-ray scattering techniques have short measurement times and require simple mathematical calculations. They do not require parameters such as X-ray production cross-section, fluorescence yield, the product I_0G (the intensity of the exciting radiation falling on the area of the target) and fractional X-ray emission rate.

Coherent scattering and Compton scattering are the most predominant photon interaction modes. The coherent to Compton scattered intensity ratio can be used to calculate the mean atomic number of the samples and to estimate the absorption coefficients in the samples (Espen et al., 1979). Singh et al. (2010) measured the effective atomic numbers of scientific (lanthanide oxides and alloys of lead and tin of known compositions) and biological samples (iodine content of tissues) using the scattering intensity ratio of 145 keV gamma rays. Cooper et al. (1982) examined the sample composition change in alloys using scattered intensity ratios. Gigante et al. (1985) analyzed metal alloys using scattered intensity ratios and X-ray fluorescence peaks in the 50–122 keV energy range. Athanassiadia (2009) determined the effective atomic number of light composite materials (textolite, textolite adust, brass, beech, polyurethane and organic glass) by measuring the relation between the intensities of the scattered peaks. Manjunathaguru and Umesh (2006) determined the effective atomic number of several biologically important compounds.

In the present work, the effective atomic numbers have been calculated for gunshot residues of a 5.56 mm × 45 mm bullet at 59.54 keV photon energies using an HPGe detector. The effective atomic numbers of the cartridge case, bullet core, bullet jacket and gunpowder are deduced from coherent to Compton scattered intensity ratio values.

2. The method of computation and theoretical basis

The theoretical Compton and coherent scattering differential cross-sections for atoms are calculated using equations such as

$$\frac{d\sigma_C}{d\Omega} = \frac{d\sigma_{KN}}{d\Omega} S(q, Z) \quad (1)$$

$$\frac{d\sigma_{coh}}{d\Omega} = \frac{d\sigma_T}{d\Omega} [F(q, Z)]^2 \quad (2)$$

where $d\sigma_{KN}/d\Omega$ is the Klein–Nishina cross-section of an electron, $d\sigma_T/d\Omega$ is the Thomson scattering cross-section, $F(q, Z)$ is the atomic form factor, $S(q, Z)$ is the scattering function and q is the momentum transferred to the electron. The coherent to Compton scattering differential cross-section ratio has a power relation to Z in the region of elemental interest and this power dependence is based upon the ratio F^2/S . $F(q, Z)$ and $S(q, Z)$ were calculated by Hubbell et al. (1975).

The coherent to Compton scattering differential cross-section ratio is calculated by weighting the atomic percentages α_j^{at} of elements by $F(q, Z)$ and $S(q, Z)$.

$$R = \frac{\sum_{j=1}^n \alpha_j^{at} |F(q, Z_j)|^2}{\alpha_j^{at} S(q, Z_j)} \quad (3)$$

where α_j^{at} is defined by atomic percentage w_j and atomic mass A_j of the j th element as

$$\alpha_j^{at} = \frac{(w_j/A_j)}{\sum_j (w_j/A_j)} \quad (4)$$

The total atomic cross-section ($\sigma_{t,a}$) is given as

$$\sigma_{t,a} = \sigma_{t,m} \frac{1}{\sum_j n_j} \quad (5)$$

$\sigma_{t,m}$ is the total molecular cross-section and is given as

$$\sigma_{t,m} = \frac{1}{N} \sum_j \left(\frac{\mu}{\rho} \right)_j (n_j A_j) \quad (6)$$

where N is Avogadro's number, n_j is the number of atoms, A_j and $(\mu/\rho)_j$ are the atomic weight and total mass attenuation coefficient of the j th element in a molecule, respectively. The total electronic cross-section ($\sigma_{t,e}$) is given as

$$\sigma_{t,e} = \frac{1}{N} \sum_j \frac{\alpha_j A_j}{Z_j} \left(\frac{\mu}{\rho} \right)_j \quad (7)$$

where α_j is the number of atoms of element j relative to the total number of atoms of all elements in the mixture and Z_j is the atomic number of the j th element in a molecule. The effective atomic number of the composite material is given as

$$Z_{eff} = \frac{\sigma_{t,a}}{\sigma_{t,e}} \quad (8)$$

3. Experimental details

In the present experiment, the intensities of coherent and Compton scattered gamma photons are measured at a particular scattering angle. The experimental setup and the sample chamber used in the present study are shown in Figs. 1 and 2, respectively. The samples were excited at 59.54 keV gamma rays emitted from a 4.69 Ci ^{241}Am annular source. In this work, an HPGe detector is used. The HPGe detector is a DSG planar high purity germanium crystal with a diameter of 16 mm, a length of 10 mm, a beryllium window of 0.12 mm and an active area of 200 mm². A barium reference sample was positioned at the collimator of the HPGe detector.

The spectra were recorded using a Canberra (AccuSpec) PC-based multichannel analyzer card. The time constant of the Ortec model 472 amplifier was set to 6 μs , ensuring optimum detector

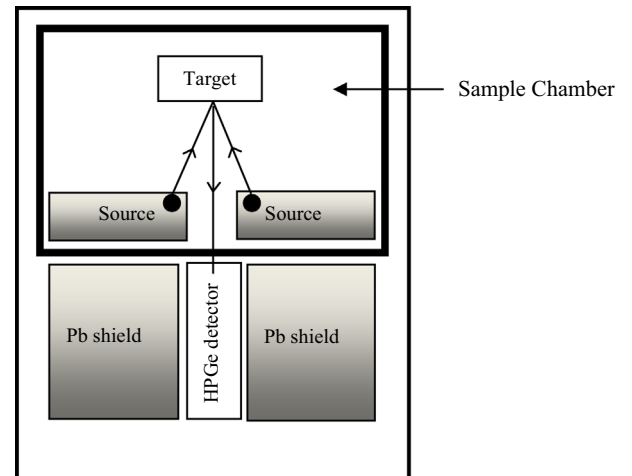


Fig. 1. Experimental setup.

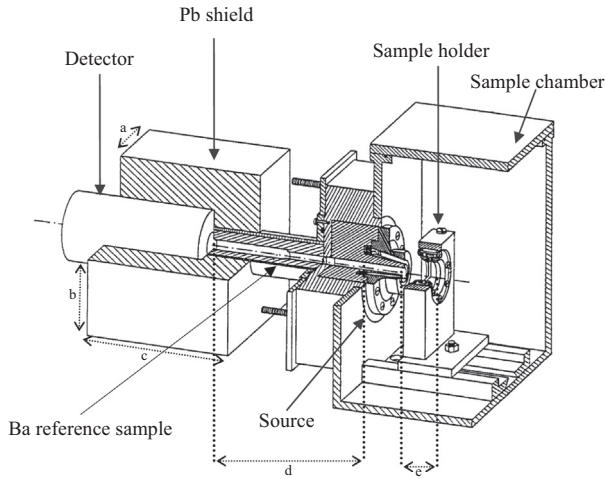


Fig. 2. Sample chamber (a=6.5 cm, b=6.3 cm, c=13.5 cm, d=11 cm, and e=5 cm).

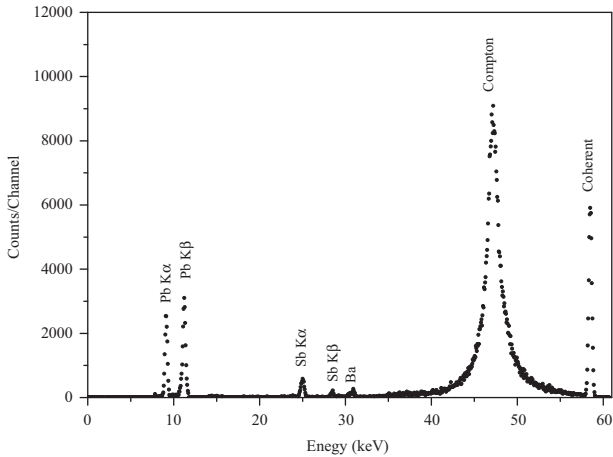


Fig. 3. A typical spectrum for the bullet core.

performance as specified by the manufacturers. The operating parameters of the system were governed and controlled by the computer program Genie-2000. The data were collected into 1024 channels of the MCA and analyzed by the Origin 7.5 software program. The typical spectra of bullet core and cartridge case are shown in Figs. 3 and 4, respectively.

4. Results and discussion

In this work, targets of known atomic number (Be, C, Al, Si, Ca, Ti, V, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, La, Dy, Yb, Ta, Au and Pb) and thickness (0.022–0.865 g/cm²) are used. The scattered spectra of the targets are recorded for a period of 3600–61200 s. The recorded background count rate was subtracted from the measurements. These observed intensities are corrected for photo-peak efficiency of the HPGe detector, absorption in the air between the target and the detector, and self-absorption in the primary target, as per the relation

$$N_{actual} = \frac{N_{obs}}{\epsilon_{\gamma} \beta_{\gamma a} A} \quad (9)$$

where N_{obs} is the observed intensity under the coherent (or Compton) peak; $\beta_{\gamma a}$ is the correction factor for absorption of photons in the air present between the target and the detector; $\beta_{\gamma t}$ is the self-absorption correction factor for the scattered photons

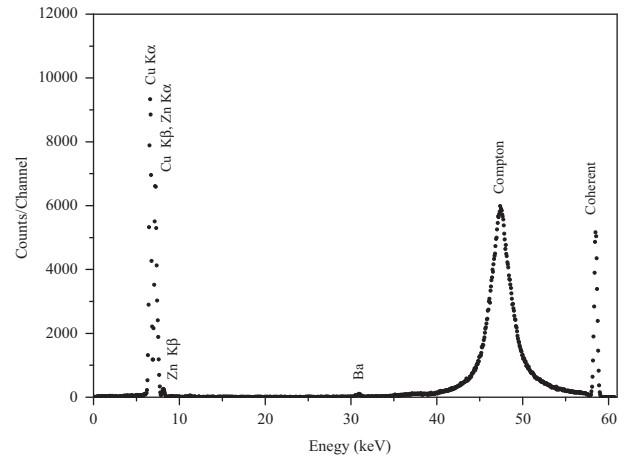


Fig. 4. A typical spectrum for the cartridge case.

in the target; and ϵ_{γ} is the photo-peak efficiency of the detector for coherent (or Compton) scattered photons. The self-absorption correction factor is given as

$$A = \frac{1 - \exp[-(\mu_1 + \mu_2)d]}{(\mu_1 + \mu_2)d} \quad (10)$$

This equation takes the simple form for scattering angles close to 180°. μ_1 and μ_2 are the absorption coefficients for the incident and scattered quantum, respectively, and d is the target thickness (Weyrich, 1975). The photo-peak efficiency curve for the HPGe detector is measured experimentally at 13.81–1212.95 keV photon energy using Am²⁴¹, Ba¹³³, Cs¹³⁷ and Eu¹⁵². Each of these radioactive sources of known activity is placed at the position of the elemental target and the energy spectra are recorded by the HPGe detector. The solid angle subtended by the detector at the center of the source is thus the same as in the actual measurements. For gamma emitted from a radioisotope source with known activity, the efficiency is given by the expression

$$\epsilon_{\gamma} = \frac{A_c}{N_0 p_{\gamma} e^{-\lambda t}} \quad (11)$$

where A_c is the net peak area in counts, N_0 the activity of the source at the time of standardization, p_{γ} the absolute gamma ray emission probability, λ the decay constant and t the elapsed time since standardization. The energies and emission probabilities of the sources used in the present work are taken from the Table of Radioactive Isotopes (Firestone and Ekstrom, 2004).

The intensity ratio of coherent and Compton scattered peaks for the targets is plotted as a function of atomic number and is given in Fig. 5. The solid curve represents the best-fit curve through experimental data points corresponding to the intensity ratio of coherent to Compton scattering in Fig. 5. The equation for the best-fit curve is

$$R = 0.05441 - 0.01043Z + 3.9937 \times 10^{-4}Z^2 \quad (12)$$

Each of gunshot residues is replaced with the elemental target, and the scattered spectra are recorded. The spectra of the gunshot residues were recorded at a duration of 7200 s. The intensities of coherent and Compton peaks are recorded. The actual intensities under these peaks are corrected with Eq. (11). The effective atomic number of the core, the jacket and the barrel of the bullet and gunpowder is then deduced from the best-fit curve of Fig. 5. It is observed that the use of calibration Eq. (12) provides an identification of gunshot residues with unknown content. Also, the effective

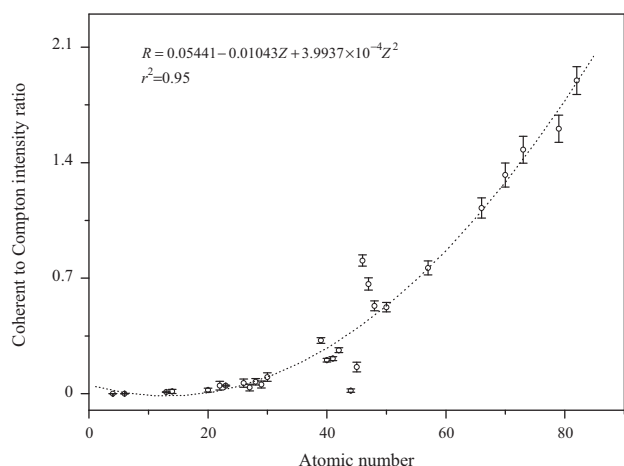


Fig. 5. Coherent to Compton scattered intensity as a function of atomic number.

Table 1
Effective atomic numbers of gunshot residues.

GSR	Effective atomic number	
	Experimental	Theoretical
Gunpowder	19.0 ± 0.5	19.9
Bullet jacket	26.8 ± 0.9	29.0
Cartridge case	27.5 ± 0.9	29.3
Bullet core	80.1 ± 4.4	81.4

atomic numbers of the gunshot residues are theoretically determined using the WinXCom program (Gerward et al., 2001).

The bullet core is composed of Pb–Sb alloy as seen from Fig. 3. Also, the cartridge case is made of Cu–Zn alloy as can be seen in Fig. 4. Modern gunpowder is based on nitrocellulose. The experimental and theoretical values of the effective atomic numbers of gunshot residues are given in Table 1. As seen from Table 1, the measured values of Z_{eff} are in agreement with the theoretical values. The contribution of coherent scattering, Compton scattering and photoelectric process to the total photon interaction can be verified using XCOM software. As seen from Table 2, Compton scattering contributes about 1.89% to the total interaction at 59.54 keV for the bullet core (Pb–Sb alloy). The overall error in the experimental parameters is the sum of the uncertainties in different factors, namely the evaluation of peak areas (1.5–3.2%), target mass thickness (1.1–3.6%), photo-peak efficiency (1.2–2.4%) and statistical error (<1.00%). The total errors affecting the experimental parameters are calculated to be between 2.5% and 5.5%.

It is clearly seen that Z_{eff} depends on the concentration of the target. In the theoretical calculations, known elemental concentration of the constituent, mixture rule and XCOM database are used. But, the database does not take into account molecular and solid-state effects and energy absorption coefficients. As seen from

Table 2
The contributions verified using XCOM to total photon interaction (%).

GSR	Coherent	Compton	Photoelectric
Gunpowder	9.99	45.30	44.71
Bullet jacket	6.70	7.98	85.31
Cartridge case	6.64	7.83	85.53
Bullet core	9.48	1.89	88.63

Table 1, the different between theoretical and experimental values can be caused by this situation.

5. Conclusions

The present experiment uses a simple non-destructive technique which involves measurement of the coherent to Compton scattered intensity in EDX to determine effective atomic number of gunshot residues. Values of Z_{eff} depend on the chemical content of the investigated gunshot residues. The agreement of the present experimental values with the theory appears to be quite satisfactory. It is an interesting issue to determine Z_{eff} of gunshot residues with scattering of gamma rays (scattered intensity ratios) in forensic science.

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