Isotopic and other investigations in relation to a safe burglary

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Summary and Introduction

Summary

Material found with a suspect was compared analytically with safe wall filling material released during a safe burglary. Both materials consist of a mixture of alum crystals and sawdust, together with metal iron containing particles. Analytical results, were combined successfully with information on the historic use of the alum/sawdust combination, alternative applications and encountered frequency during safe burglaries in the Netherlands.

Introduction

Safe wall filling material was released when an old safe was burglarized. During a search at the suspect's residence visually similar material was retrieved from a bag with money. The safe wall filling material consists of a mixture of alum crystals (XRF/XRD) and sawdust (vis, FT-IR). Small iron-containing particles were also present. In this poster results will be presented for 'classical' as well as for IRMS investigations on the sawdust (H, C, O) and alum (S) fractions.

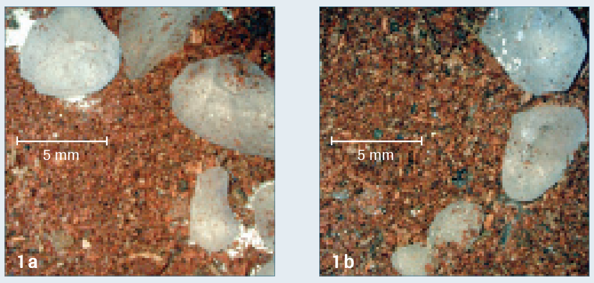


Fig 1. (a) material in plastic bag with money at suspect's house and (b) safe wall filling as found at crime scene

Sawdust fraction – visual, botanical and FT-IR results

Photographs of the samples are shown in Fig. 1. The white glass like lumps in the photographs are alum. Dimensions of these alum crystals (some mm up to 10 mm) are much larger than the standard alum obtained from lab chemical suppliers (typically < 1 mm).

The samples from Fig. 1a and 1b will be referred to as the suspect and the crime scene samples, respectively. Both sawdust samples are visually similar and have the same red brown colour. This colour differs from ten other Dutch red brown sawdust samples collected as reference materials.

Initial botanical species investigations on sub-samples of the possible sawdust fractions at the National Herbarium of the Netherlands confirmed the sawdust nature. A mixture of wood species, both soft and hard woods, was observed in both samples. Over 5 species were identified in the suspect sample. A large-scale investigation is required for comparison but has not been done yet.

The FT-IR-spectra for sub-samples of the sawdust fraction were very similar for both samples and comparable to the FT-IR spectrum of cellulose.

Alum / metal – XRF, XRD, ICP AES and ICPMS results

Alum

The glass like particles in Fig. 1a and b were classified as alum or potassium alum (KAl(SO4)2.12H2O) using XRF and XRD.

ICP AES results were obtained using a PE OPTIMA 3000 instrument. Apart from the major elements Al and K (S was not measured), Cr and Tl were observed at similar levels in both samples. Other elements observed (Fe, Sr,..) were present at much higher concentrations in the red-brown powder so that these are not yet confidently attributed to the alum samples.

Preliminary LA ICPMS results using a PE ELAN 6100 DRC PLUS instrument were obtained on freshly cleaved alum crystal surfaces. Elements observed in both samples are Mg, Si, P, Ti, Cr, Cu, Zn, Ga, Rb, Sr, Sn, Ba, Tl and Pb. Signal intensities varied for different crystals within a single sample, making discrimination between samples difficult.

Metal particles

In both samples many minute metal particles were observed that were magnetically separated from the sample matrix. Corresponding variations in morphology of the particles (round balls of various sizes and curved lint like particles) indicate that metal particles in the two samples were formed through a similar process. µ-XRF (EAGLE) results for the round balls and lint particles show a high abundance of Fe as well as the presence of other elements such as Al, Si, P, S, Mn and Cu. Similar results were obtained for the minute metal particle fractions in both samples from Fig. 1a and 1b.

Further experimental details are available upon request.

IRMS – background/experimental

Background IMRS

For many elements (H, C, N, O, S,...) several stable (non-radioactive) isotopes are present in the materials we encounter. Relative isotope shifts δ [1] of these elements vary measurably in the materials around us through physical, chemical and biological processes. They offer therefore potential for forensic comparison of materials.

δ is defined for C as:
$\delta^{13}C$ (‰) = $(R_{smpl}/R_{std}-1) \times 1000$
with R_{smpl} = $^{13}C/^{12}C$ of a sample and R_{std} = $^{13}C/^{12}C$ of an international standard.

Experimental

IRMS services were provided by Iso-Analytical Ltd (Sandbach, UK) using standard methods on a Europa Scientific Geo 20-20 instrument with an EA-IRMS interface. Samples were dried before analysis to remove moisture. The various isotope ratios were measured in separate experiments using different experimental configurations of the instrumentation. Depending on the isotope ratio to be measured 0.3 - 1.5 mg sample amounts were used in the analysis. Reference samples and quality control samples were also measured.

Further IRMS experimental details are available upon request.

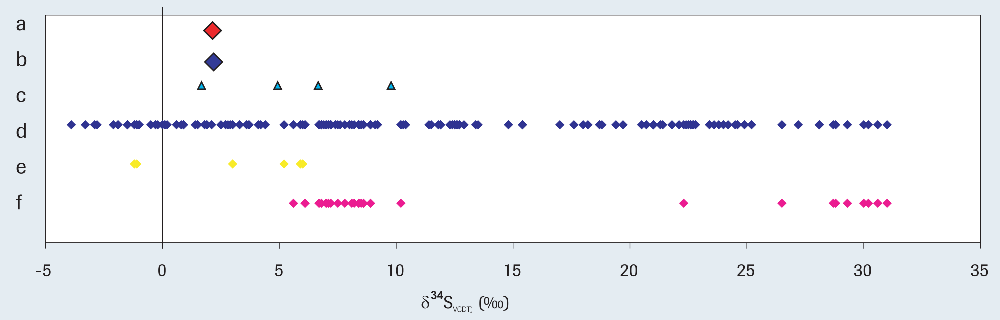
IRMS – results/interpretation alum

The mean $\delta^{34}S$ values are 2.21 ± 0.12 ‰ and 2.19 ± 0.12 ‰ (n = 6) for the suspect and the crime scene alums, respectively. Using a measurement uncertainty of 0.24 ‰ (2s) the alum samples are therefore undistinguishable in these measurements. To be able to interprete the significance of this result, ideally the frequency distribution of $\delta^{34}S$ for alum materials encountered in the Netherlands and unrelated to the present safe burglary should be known. We tried to approximate this below.
Alum can be obtained from naturally occuring minerals (e.g. alunite) or produced in a number of chemical (industrial) syntheses. A variation range of -3.9 to +30.6 ‰ was reported [2] for $\delta^{34}S$ values obtained for a number of alum minerals from various locations throughout the world.

In Fig. 2d these values are presented together with the values for the crime scene and the suspect alums in Fig. 2a and 2b. To indicate the actual wide $\delta^{34}S$ variation, in Fig. 2e and 2f alum $\delta^{34}S$ values are plotted for two Spanish mines (Riaza and Rodalquilar) where these alum minerals are found. No data was found in the literature on $\delta^{34}S$ variation for chemically synthesised alums. Four different alum samples supplied in the Netherlands by Acros and Fluka were therefore also investigated. $\delta^{34}S$ values are plotted in Fig. 2c and indicate again the wide variation range for this parameter.

On the basis of these results the alum $\delta^{34}S$ variation for Dutch alum samples is approximated by the range as reported in Fig. 2d : -3.9 to +30.6 ‰.

Fig 2. Alum $\delta^{34}S$ variation (a) safe, (b) suspect, (c) Dutch Alum samples, (d) alunite data from minerals - worldwide, (e) alunite Spain - Riaza and (f) alunite Spain - Rodalquilar



Information alternative scenario's

The alum/sawdust material combination appears very rare. To better test for alternative hypotheses information was collected on:

1. The history of the alum/sawdust use as safe wall filling
2. Alternative applications of this material combination
3. The frequency of encounter by the Dutch police organisations of this material since 1 januari 2002

Results

1. The safe was produced by the London firm of Chatwood, acquired in 1958 by Chubb. No production information was available anymore. Both through Chubb and by information of other safe manufacturers it was deduced that the alum/sawdust material combination was only used for wall filling of safes and fire resistant cupboards in the period before World War II
2. Although there are some applications where alum is used separately, no alternative applications were found where the alum/ sawdust combination was used
3. All 25 Dutch police forces were interviewed. From the 20 responding police forces nobody had encountered this material

IRMS – results/interpretation sawdust

Fine sawdust fractions were prepared by magnetic removal of the metal particles and retrieving visually different particles (such as the alum crystals) from the sawdust. H-, C- and O- isotope ratios were measured for the fine sawdust fractions. Results are presented in table I.

Table I
Isotope ratios for suspect and crime scene sawdust sample fractions (n=6)

Isotope	Suspect	Crime scene
$\delta^{2}H$ (‰)	-79,22 + 3,52	-81,19 + 3,20
$\delta^{13}C$ (‰)	-25,71 + 0,15	-25,73 + 0,07
$\delta^{18}O$ (‰)	24,01 + 0,47	23,65 + 0,21

The results in Table I show that the sawdust fraction isotope ratios $\delta^{2}H$, $\delta^{13}C$ and $\delta^{18}O$ for both the suspect and the crime scene samples agree within the experimental uncertainty (2s). It should be noted that no chemical derivatisation (e.g. nitration) was applied to exchange labile H-atoms in the OH groups and exclude H-exchange with atmospheric moisture.

To interpret the significance of the results we need to obtain information on the frequency distribution of the $\delta^{2}H$, $\delta^{13}C$ and $\delta^{18}O$ for sawdust encountered in the Netherlands and unrelated to the present safe burglary. For most tree species carbon dioxide is assimilated through the C3 photo-synthetic route. For these C3 plants $\delta^{13}C$ values in the range of -32 to -22 ‰ have been reported [3]. As an indication for the Dutch situation a number of different sawdust samples (both tropical hard woods, teal, wood mixtures etc.) were collected in the Netherlands and analysed by IRMS ($\delta^{2}H$, $\delta^{13}C$ and $\delta^{18}O$).

In Fig. 3 the $\delta^{13}C$ and $\delta^{18}O$ values are plotted for the casework samples as well as for the reference sawdust samples. A wide variation for the $\delta^{13}C$ and $\delta^{18}O$ values is already observed using this limited set of reference samples. Assuming a continuous varying frequency distribution for $\delta^{13}C$ and $\delta^{18}O$ values and using the measurement uncertainty (2s) of 0.3 ‰ for $\delta^{13}C$ and 0.9 ‰ for $\delta^{18}O$, a wide range of $\delta^{13}C$ / $\delta^{18}O$ value combinations are possible. These can be well discriminated using this method.

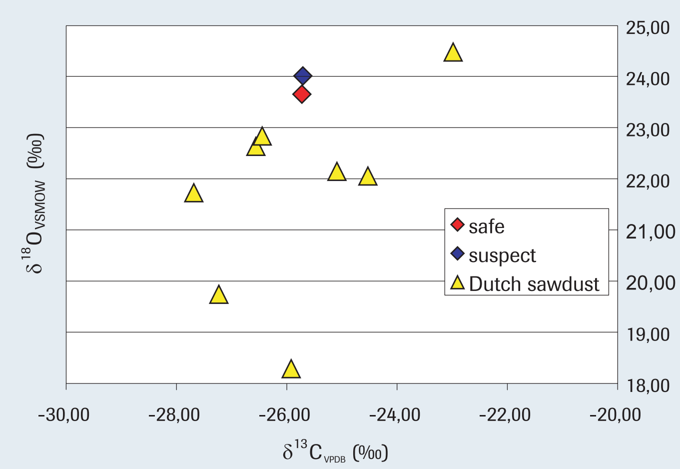


Fig 3. $\delta^{13}C$ and $\delta^{18}O$ of casework samples and Dutch sawdust samples

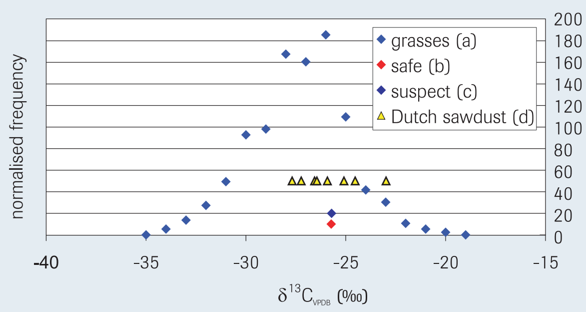


Fig 4. Variation $\delta^{13}C$ for (a) grasses worldwide, (b) safe, (c) suspect and (d) Dutch sawdust samples. For (b), (c) and (d) disregard frequency axis.

In Fig. 4 the $\delta^{13}C$ values for the casework samples and for the reference sawdust samples as well as for literature data on the frequency distribution of $\delta^{13}C$ values for C3 grasses [3] are plotted. Our casework samples appear at the center of this distribution and the values for the Dutch sawdust reference samples provide a similar spread as observed in the distribution for the C3 grasses.

Conclusions

Combining the information from the various sources and the analytical results for the various material fractions (sawdust, alum, metal particles) provides a strong discriminating method to compare the material fractions in the samples at the suspect's residence and at the scene of crime. IRMS is demonstrated to be a very useful and discriminating method by combining S isotope ratios for the alum and H, C and O isotope ratios for the sawdust fractions. An extensive literature study was required to interpret and substantiate the significance of the IRMS results. A limited reference sample set was required to test applicability of the literature information to the Dutch situation.

References

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