B166 IRMS and ICPMS Studies on Packaging Tapes

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After attending this presentation, the participant will appreciate the strong potential of the combination of ICPMS and IRMS techniques, not only for tape investigations but for a wide spectrum of forensic investigations.

This presentation will demonstrate new interesting forensic applications of the (LA-)ICPMS and IRMS elemental and isotopic techniques presently developed. They promise to result in much more strongly discriminating methods for forensic applications. The subject in the present presentation is just one of these applications but is very useful in demonstrating the relevance of these techniques. The relevance is also recognized by the two international forensic networks that have become active in this field: NITECRIME and FIRMS. More information on these networks can be submitted if requested.

Results are presented for tape comparison experiments using the novel forensic IRMS (Isotope Ratio Mass Spectrometry) technique. Results will be discussed and compared with results using other new forensic techniques such as solution nebulisation ICPMS and LAICPMS.

Introduction: Brown packaging tape is encountered in 60% of the violent crimes (murder, rape) committed in The Netherlands where tape is found at the crime scene. Normally, the forensic scientist is asked to compare the tape retrieved from the crime scene with tape found with a suspect. At the NFI a combination of visual investigation (physical fit, tape dimensions, colour, morphology), FT-IR and XRF is used routinely to compare tapes. FT-IR can be used to identify the type of glue and backing polymer. A combination of visual comparison and XRF analysis generally suffices to discriminate between different tape products but cannot be used for further discrimination between different batches of one brand of tape product.

Solution: ICPMS In earlier studies, the more varying adhesive layers of the tapes were investigated using both solution nebulisation ICPMS (Inductively Coupled Plasma Mass Spectrometry) and LAICPMS. With these techniques trace levels of elements are detected and identified. Solution nebulisation ICPMS experiments, especially, produced very discriminatory results. A ThermoFinnigan HR-ICPMS was used. For solution nebulization measurements, the glue (*ca* 50 mg) was first separated from the backing material through mobilisation in a solvent (methanol, hexane) and then digested in a microwave oven (75 bar, 290 ºC) in a nitric acid/H_2O_2/H_2O mixture. For the three different brands investigated, commercial samples from the same tape product acquired at different times from one commerical outlet and at one time from different outlets could be discriminated on the basis of the solution nebulisation ICPMS results whereas visual comparison and XRF (macro elements) were not sufficient for discrimination between these tapes.

LA ICPMS Laser ablation measurements on intact tape samples of the above rolls were made directly on the glue layer using a 266 nm Nd:YAG laser. Tape samples were placed in the sample chamber and the glue layer was laser ablated. Volatiles and aerosols produced in this way were swept into the ICPMS system (low mass resolution mode). As optimal values a laser pulse energy of 2 mJ, a pulse repetition rate of 10 Hz, a spot size of 80 µm and an ablation distance (lateral shift of laser spot) of 30 µm were chosen. Laser spots were therefore partially (50 µm) overlapping. Signals were integrated for 60 seconds over a grid area of 1 mm^2.

LA ICPMS results for the different rolls of one brand of tape demonstrate for each brand that discrimination power is sufficient to discriminate the rolls but is somewhat lower relative to solution nebulization results. In these experiments all tapes could be discriminated. Upon repetition of the LA ICPMS experiments for the three different rolls of one brand on another day the same distribution pattern is observed. The exact location of the distribution pattern is not exactly the same however, reflecting in our opinion variations in laser pulse energy observed during these specific experiments.

IRMS (Isotope Ratio Mass Spectrometry) focuses on stable isotope ratios of abundant elements in the samples such as H, C and O (O only in the oxygen containing materials). Isotope ratios used were $^2H/^1H$, $^{13}C/^{12}C$ and $^{18}O/^{16}O$. Tape samples were analysed for us at IsoAnalytical Ltd (Sandbach, Cheshire CW11 3HT, UK). The IRMS used was a Europa Scientific Geo 20-20 instrument. All samples were measured in triplicate. Tape samples were prepared for analysis by separating the glue and backing layers which were analysed separately. Also complete tape samples, without further sample preparation, were analysed.

IRMS Conditions: Hydrogen isotope analysis (ca. 6 mm^2 tape sample) was conducted by total conversion at 1080 ºC in a quartz reactor lined with a glassy carbon film, filled to a height of 180 mm with glassy carbon chips. Hydrogen was separated from other gaseous products on a GC column packed with molecular sieve 5A at a temperature of 30 ºC. A Faraday cup collector array was used to monitor the masses 2 and 3. Carbon isotope analysis (ca. 5 mm^2 tape sample) was conducted by EAIRMS using a combustion furnace, reduction furnace and GC oven temperature of 1000, 600 and 90 ºC, respectively. Oxygen isotope analysis (ca. 22 mm^2 tape sample) was conducted by total conversion at 1080 ºC in a quartz reactor tube lined with a glassy carbon film, filled to a height of 170 mm with glassy carbon chips and topped with a layer (10 mm deep) of 50% nickelised carbon. Carbon monoxide and nitrogen were separated on a GC column packed with molecular sieve 5A at a temperature of 50 ºC.

Excellent IRMS results were obtained. For the three different

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brands investigated, commercial samples from the same tape product acquired at different times from one commerical outlet and at one time from different outlets could be discriminated on the basis of a combination of the $\delta^{13}C$ and $\delta^{2}H$ results. Alternatively, for the two oxygen containing brands, samples could easily be discriminated using a combination of the $\delta^{13}C$ and $\delta^{18}O$ results. This could be done using either results for the full tape, the glue or for the backing material. Especially the latter is of great value since this means that, together with the glue, all other debris (blood, hairs, fibers) can easily be removed.

Discussion: Comparing IRMS with ICPMS an interesting characteristic is that whereas ICPMS focuses mostly on trace elements and is therefore inherently more sensitive to contamination, IRMS focuses on the abundant elements (H, C and O) in organic chemical samples and therefore is less sensitive to contamination problems. The above results demonstrate the strong potential of novel forensic techniques such as (LA-)ICPMS and IRMS for forensic investigation of packaging tapes. In our expectation this will prove to be only one example of a wider forensic application of these techniques for forensic material comparisons.

Tape, ICPMS, IRMS