ELEMENTAL COMPARISON OF PACKAGING TAPES USING HR ICP/MS

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ABSTRACT: Brown packaging tapes were characterised using High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP/MS) as well as microscopic, FT-IR and XRF methods. Tapes from various producers and tapes of one brand but acquired in different commercial outlets at the same time could be discriminated upon analysis of the adhesive layer by HR ICP/MS (elements V, Cr, Co, Mn, Ni, Cu and Zn). Furthermore tapes from two different production batches could be discriminated.

INTRODUCTION

Tape fragments are encountered at various crime scenes. Frequently the forensic scientist will be requested to compare the tape encountered at the crime scene with tape found with a suspect. Presently used techniques [1] are visual investigations (physical fit, tape dimensions, colour, morphology), FT-IR (typing backing layer and adhesive layer), Py-GC (MS) (characterisation of backing layer and adhesive layer) and XRF (elemental analysis).

The discriminating power of these combined methods is limited however. FT-IR is used to determine the class of adhesive and backing material used [1, 4, 8, 9]. More detailed organic information (e.g. small amounts of co-monomers in acrylate adhesives) can be obtained using Py-GC/MS [8, 9, 12]. A combination of FT-IR with visual comparison and XRF analysis suffices to discriminate different brands of tapes but generally cannot be used for further discrimination between different batches from one brand of tape [1].

Interesting elemental information has been obtained in the past using neutron activation analysis (NAA) [11] and glazing incidence X-ray fluorescence analysis [7].

However, because of their highly specialised character, the need for expensive equipment and the necessity of a nuclear reactor for NAA these techniques are not widely applied within the forensic community.

In this article the focus will be on the potential of High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP/MS) [6]. It will be demonstrated that this ultra-sensitive elemental technique offers a major step forward in forensic tape investigations by determining profiles of trace elements present in the tapes. The higher resolution possible, compared to quadrupole ICP/MS, means certain spectral interferences can be avoided thereby simplifying the measurement of certain elements. Furthermore, the technique can be coupled to Laser Ablation (LA HR ICP/MS) for micro analysis (20–400 µm dimensions).

Various kinds of tapes (packaging tape, black PVC insulation tape, duct tape) are of forensic interest. This study will be limited to brown packaging tapes as encountered in the Netherlands in over half of the investigations where tapes are found at a crime scene.

Tapes of three brands were acquired at different commercial outlets and at different times.

In the second stage of the investigation tapes from two different production batches were supplied by a manufacturer and were investigated.

PACKAGING TAPE LAYER STRUCTURE AND POSSIBILITIES FOR CHARACTERISATION

In essence, packaging tapes consist of a backing film and an adhesive layer for which a Pressure-Sensitive Adhesive (PSA) [2, 3] is used. PSA is a viscoelastic material which, in solvent-free form, remains permanently tacky at room temperature. The basis of PSA's is often a polymer which in itself is not tacky enough e.g. natural rubber [10]. Tackifying resins based on rosins, petroleum or terpenes are therefore added, along with hydrogenated resins to help in long term ageing [3]. Pigments and additives are added to improve tape characteristics and appearance. In past XRF and ICP OES experiments it was determined that relatively high elemental concentrations of Fe (iron oxides for brown colour, typically 2% m/m), Ti (from TiO_2, a widely used opaqifier and typically present in concentrations of up to 10% m/m) and sometimes Si (from silicates which are used as additives) are present in the adhesive.

For the backing film of packaging tapes, currently, biaxially oriented polypropylene (BOPP) is mostly used [2]. Only a few BOPP manufacturers supply all tape producers.

The backing film is primed with a primer layer (2–5 g/m^2) for improved adherence of the adhesive layer to the backing film. Nitrile rubbers, chlorinated rubbers or acrylates are mainly used for this.

A release coating (1–5 g/m^2) is applied on the back side of the backing film. During unwinding the tape roll this coating assists in reducing unwind tension and preventing adhesives from another winding sticking to the back side of the tape. Acrylic esters of long chain alcohols and cellulose esters are used for this coating.

To summarise, the tape is structured as follows (starting at the back of the tape): release coating/backing film/primer layer/PSA adhesive layer.

In principle all these separate layers can be investigated. In practice however it will be difficult to isolate e.g. the primer layer.

Two investigational routes were pursued in this study:
– the whole tape is investigated without separation of the tape layers,
– the adhesive layer is sampled and investigated.

EXPERIMENTAL

The investigation described in this article consists of three parts:
1. Determining optimal conditions for digestion of tapes and HR ICP/MS experiments;
2. Measuring samples of three brands of tape to determine discrimination power;
3. Measuring samples of two tape production batches to determine intra and inter batch variation.

Tape samples studied

Three brands of brown packaging tapes were acquired at different shop outlets and at different times in the towns of Leidschendam and Zoetermeer, in October 1996 and September 1998:
– Tesa 4024 from the DIY-chain of Gamma;
– Own brand of the V&D chain of department stores;
– Ruban Embal brand from the chain of Blokker shops.

The above tape samples were characterised microscopically, with FT-IR to type backing and adhesive layers and with XRF to determine macro elemental composition.

Furthermore twelve rolls of Tesa 4024 rolls from two different production batches in 2000 (2 × 6 rolls) were supplied directly by the manufacturer of Tesa. These rolls were used to determine intra and inter batch variation.

As experimental control, a sample of tape from a dedicated Tesa 4024 roll was prepared and analysed in each analytical run. This roll was also used in the method development experiments.

Experimental equipment

Removal of the adhesive from tape samples was performed inside a laminar flow bench (Interflow, class 100).

A Multiwave Sample Preparation System (Anton Paar Physica, Graz, Austria) was used for microwave digestion of the adhesive and complete tape samples. Both TFM and quartz lined closed reaction vessels were used. These two types of digestion vessels have different physical and chemical properties, the most important being that with TFM vessels 260°C and 30 bar can be used, cf. 300°C and 75 bar for quartz vessels. TFM vessels on the other hand are necessary if HF is used as a digestion reagent since HF will react with quartz.

For the HR ICP/MS-experiments a Finnigan Element system was used (Figure 1). The sample is introduced as a liquid via a nebulizer into a spray chamber where an aerosol is produced for transport into the hot ion plasma of the Inductively Coupled Plasma (ICP). Ions are sampled from this plasma and enter the mass spectrometer.

The Element mass spectrometer is a high resolution double sector instrument with reversed Nier-Johnson geometry. In high resolution (HR, $M/\Delta M$ >10000) already sensitivies of $> 5 \times 10^3$ cps/ppb are obtained for K (transmission 2%). In low resolution (LR, $M/\Delta M = 300$, comparable to quadrupole) this rises with about two orders of magnitude to e.g. $> 5 \times 10^5$ cps/ppb for In and $> 5 \times 10^6$ cps/ppb for U. In our experiments low and medium resolution (MR, $M/\Delta M = 4000$) were sufficient.

For auxiliary experiments a Spectro X-Lab 2000 system was used for EDXRF measurements, a Perkin Elmer Optima 3000 system was used for ICP-OES measurements and a Bruker ITS 45 system was used for FT-IR measurements.

Sample preparation

For optimisation of the experimental conditions samples were taken from one dedicated Tesa 4024 roll which was also used for control samples in subsequent experiments on other tape samples.

Adhesive removal

About 10 cm² of tape was sampled. Margins of 2 mm on both sides were discarded so as to prevent contamination on the side edge of the roll from influencing the analytical results.

Fig. 1. High resolution sector ICP/MS system.

Experiments were performed using both the complete tape and only the adhesive.

For the latter experiments the adhesive was removed after first mobilising the adhesive with 0.5 ml of a suitable solvent. After initial experiments methanol was selected as most optimal from a selection of methanol, acetone, hexane and dichloromethane. The mobilised adhesive was scraped off the backing layer and dried overnight in a dust free hood.

Digestion

For microwave digestion of tape samples, both TFM vessels (HF resistant) and quartz vessels (not HF resistant) were used depending on the reagents. Various mixtures of digesting reagents were studied consisting of hydrogen chloride, hydrogen fluoride, hydrogen peroxide, nitric acid and water in varying combinations. Destruction time interval at specific temperature was optimised and the microwave reproducibility with respect to time of destruction and carousel position (potential hotspots within the cavity) was determined.

Optimal conditions determined in this way were used for all further tape experiments.

For sampling of the tapes an experimental design was used to discern influences of variation of experimental conditions (contamination when sam-

pling the adhesive, digestion conditions, ICPMS conditions). For each roll of tape four samples were taken in two pairs at different days. Each pair was digested in a sample carousel together with four other samples (including a control sample and a procedural blank).

RESULTS

Influence of various sample preparations

Influence of digestion mixtures for both adhesive layer and complete tape

For an optimal digestion preferably a clear and colourless solution will be obtained.

If the transition metal (e.g. Fe) content is high then the solution can be yellow. A clear colourless solution is not a guarantee of a total destruction but normally is a minimum requirement.

Complete matrix destruction of the whole tape can be achieved when the tape is folded up inside the digestion vessel and a mixture of HNO_3, H_2O_2 and HCl is used. This does not result in a complete dissolution of the sample. The high Ti content results in extensive precipitation of, most likely, TiO_2. XRF results on this precipitate showed that Ti and Fe were the major elements in this precipitate. To obtain complete dissolution, HF has to be added to the digestion mixture. HNO_3 and H_2O_2 alone are not sufficient to digest the whole tape.

After physical separation of the adhesive from the backing film, a digestion mixture of 5 ml HNO_3, 3 ml H_2O_2 and 2 ml H_2O is sufficient to achieve complete matrix destruction. Again, HF is needed if all Ti is to be dissolved. The following elements are present in the adhesive layer at concentrations of 2–100 ppm: V, Cr, Co, Mn, Ni, Cu and Zn.

From the above it is clear that more extreme conditions are necessary for digestion of the whole tape than for digestion of the adhesive layer alone. Under these conditions, with the inclusion of HCl in the digestion mixture, in the LR mode well known mass interferences are observed at m/z = 51 (^{51}V with $^{35}Cl^{16}O$) and at m/z = 53 (^{53}Cr with $^{37}Cl^{16}O$). In the MR mode these interferences should be resolved but using HCl in the digestion mixture we still observed mass interferences which were not further interpreted in this mode.

In separate experiments also the BOPP carrier of the tape was investigated after removal of the adhesive layer. Consistently very low elemental concentrations were observed. From these experiments it is estimated that

in the whole tape digestion experiments elemental contributions from the backing layer are minor relative to the adhesive layer.

Together with the small number of BOPP-suppliers for tape production it was concluded not to be effective and efficient to further pursue the whole tape digestion experiments; the choice was made to subsequently limit the study to the tape adhesive layer. HCl (necessary for the breakdown of the whole tape) was therefore excluded from the digestion mixture.

Influence digestion in TFM (using HF) vs. digestion in quartz

A quartz vessel would be preferable if all other conditions were equal, because of the superior digestion temperatures and pressures which can be used. However, HF, and therefore a TFM vessel, is necessary to dissolve the white residue (most likely TiO_2) completely.

Interestingly, using HR ICP/MS for most relevant elements very similar relative elemental concentrations of the clear solutions are observed upon comparing digestion results using a TFM vessel (with HF) and using a quartz vessel.

For ^{66}Zn using the LR mode a higher signal was obtained when using the TFM vessels. Because of the high Ti concentrations interferences of Ti compound ions may be responsible, e.g. both $^{50}Ti^{16}O$ or $^{49}Ti^{16}O^1H$ interfere at m/z = 66 with ^{66}Zn. Using the MR mode these interferences were resolved and no increase was observed in the ^{66}Zn signal when using the TFM vessels.

During a period of four months an experimental control tape sample was prepared and analysed under identical conditions as the other tape samples. The variation in relative elemental concentrations of this sample was found to be very limited indicating either no discriminatory inclusions were present in the undissolved TiO_2 or at least a reproducible inclusion had occurred.

From the above it was concluded to use the quartz vessel and no HF in the digestion mixture.

Using optimal digestion conditions elemental results using medium ($M/\Delta M = 4000$) and low ($M/\Delta M = 300$) mass resolution were compared to infer potential mass spectrometric interferences. It is preferable to use the lowest resolution possible for specific mass so as to be as sensitive as possible. Under our optimal conditions it was found that for Mn, Cr, Ni, Co and Cu low mass resolution was sufficient. For ^{66}Zn it was necessary to use medium mass resolution.

Optimal sample preparation and ICP/MS conditions

Best sample preparation results were obtained upon mobilising ca. 10 cm^2 of the adhesive layer in methanol. The material is removed and the methanol evaporated. The adhesive sample is then digested in a quartz vessel using a mixture of 5 ml HNO_3 (65%, Merck Suprapur), 3 ml H_2O_2 (30%,

Merck Suprapur) and 2 ml H_2O. A heating program of 700 W during 12 min, 1000 W during 20 min and a subsequent cooling during 35 min was used. Under these conditions a maximum temperature of 300°C and a maximum pressure of 75 bar was reached.

The digested solution was diluted a factor of 30 using Milli Q water before ICP/MS analysis so as to achieve an analyte and acid concentration compatible with ICP/MS.

Medium mass resolution experiments were performed using the elemental isotopes: ^{51}V, ^{52}Cr, ^{53}Cr, ^{59}Co, ^{55}Mn, ^{58}Ni, ^{63}Cu, ^{65}Cu and ^{66}Zn. The aim of this study is not to determine exact elemental concentrations in the adhesive layer, but as an indication estimated concentrations are given below for the Tesa 4024 control tape.

TABLE I. ELEMENTAL CONCENTRATION (INDICATIVE VALUES) IN ADHESIVE LAYER OF TESA 4024 CONTROL TAPE

Isotope	[µg/g] adhesive
V	3
Cr	23
Mn	49
Co	2
Ni	10
Cu	27
Zn	16

Method discrimination power using samples of three brands of tape

Visual, FT-IR and XRF results

Clean large pieces of brown packaging tapes of different brands can already often be discriminated visually through colour comparison. All three brands studied in the present study could be discriminated in this way. No further visual discrimination could be made between tapes of one brand.

FT-IR results showed that for tapes of all these brands a polypropylene backing film was used. The adhesives used for the Tesa 4024 and the V&D tapes were an acrylic type and could not be further discriminated using FT-IR. The adhesive used for the Ruban Embal tape was a rubber type.

XRF-results are presented in Figure 2. Elemental ratios of S/P vs. Ti/Fe are plotted for all tapes. Clearly not only can the brands be discriminated but there is also a partial discrimination within brands. For the XRF experiments complete tapes were examined. In separate XRF experiments it was demonstrated that, for these tapes, the measured elements were present in the backing layer at such low concentrations compared to the adhesive layer that the signal contribution from the backing layer could be neglected.

Fig. 2. Elemental ratios for the three brands of tapes as determined in XRF-experiments (X-Lab 2000).

Using the combination of these "classical" methods it is clear that not only can different brands of tape be discriminated but even partial discrimination within one brand of tape is possible sometimes.

ICP/MS results for samples of three brands of tape to determine discrimination power

Elemental concentrations were measured using the optimised method described above and using solution elemental standards. For each roll of tape four adhesive samples were taken. Each adhesive sample was further digested and measured separately.

Ratios of elemental concentrations are plotted below. Elemental combinations were optimised for best discrimination.

In Figure 3 ^{60}Ni/^{63}Cu vs. ^{53}Cr/Mn results are presented for the V&D tapes.

For comparison purposes 11 results for the control Tesa tape (acquired over a four month period) are included. V&D tapes acquired at the same day at commercial outlets in the towns of Leidschendam and Zoetermeer in the same region (7 km apart) could be discriminated. Also tapes acquired at one commercial outlet in different periods could be discriminated. Furthermore the relatively small variation in the results for the control samples indicates a good repeatability of the method.

Fig. 3. ICP/MS-concentration ratio (60Ni/63Cu ratio is plotted vs. 53Cr/Mn) obtained using the adhesive layer of V&D tape samples as acquired in Zoetermeer and Leidschendam in 10-96 and 9-98.

Fig. 4. ICP/MS-concentration ratio (60Ni/63Cu ratio is plotted vs. 53Cr/Mn) obtained using the adhesive layer of Tesa 4024 tape samples as acquired at Gamma in Zoetermeer and Leidschendam in 9-98.

Fig. 5. ICP/MS-concentration ratio (60Ni/63Cu ratio is plotted vs. 53Cr/Mn) obtained using the adhesive layer of Ruban Embal tape samples acquired at Blokker shops in Voorschoten and Leidschendam in 10-96 and 9-98.

Similar results are shown for the Tesa tapes acquired at Gamma (Figure 4) and the Ruban Embal tapes acquired at Blokker (Figure 5).

For each brand tape samples from the different rolls of tape can easily be discriminated using our ICP/MS method.

In conclusion ICP/MS appears to be a very powerful method to discriminate between tapes of one brand. The results indicate that it may be possible to differentiate between tape production batches.

Method discrimination power using samples of two tape production batches

To investigate the extent of differentiation of tapes using the ICP/MS method, samples from different production batches of Tesa 4024 were obtained directly from the manufacturer of Tesa. Samples of five rolls from one batch were compared with samples from five rolls of a different production batch. The ^{63}Ni/^{63}Cu vs. ^{53}Cr/Mn results are presented in Figure 6 and demonstrate that the samples of the two batches could be discriminated.

These results further substantiate that the ICP/MS method can be used for discriminating between different tape production batches. Samples from within one batch and from one roll of tape could not be further discriminated.

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Fig. 6. ICP/MS-concentration ratio (60Ni/63Cu ratio is plotted vs. 53Cr/Mn) obtained using the adhesive layer adhesive layer of Tesa 4024 tape samples from two different production batches (batch 1 and batch 2) as submitted by Tesa producer Beiersdorf.

CONCLUSION

Various individual packaging tape rolls from the same brand acquired in different shop outlets at one time or at different times could be discriminated on the basis of the ICP/MS results (using elements V, Cr, Mn, Co, Ni, Cu, Zn) whereas visual comparison and XRF (macro elements) were not sufficient for discrimination between these tapes. For one brand of tape rolls from two different production batches were also discriminated.

The results from this study demonstrate the high discrimination power of the HR ICP/MS technique for forensic investigation of tapes.

Presently, in a follow up study a Laser Ablation HR ICP/MS method is being developed to facilitate the sampling of smaller clean tape areas and reduce sample preparation time. We shall also study the influence of dirt and body materials on the results.

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