

# Sector field ICP-MS applied to the forensic analysis of commercially available adhesive packaging tapes

Andrew M. Dobney, Wim Wiarda, Peter de Joode and Gerard J. Q. van der Peijl\*

Netherlands Forensic Institute, Postbus 3110, GC 2280 Rijswijk, The Netherlands.  
E-mail: G.van.der.Peyl@nfi.minjus.nl

www.rsc.org/jaas

Received 7th January 2002, Accepted 5th March 2002

First published as an Advance Article on the web 3rd April 2002

An analytical method to determine trace element concentrations and their ratios in the glue of brown PSA packaging tapes is described. The method relies on acid digestion in quartz vessels inside a closed microwave unit and measurement by sector field ICP-MS. This methodology was applied to nine tape rolls purchased from three different shops of three different chain stores. It was possible to discriminate both between brands and within brand for all three brands. In the case of one brand, for rolls originating from the same product line but from different production batches, it was shown that the 'between batch' difference is detectable whilst there is no statistically significant difference within rolls from the same production batch. This combination of 'between batch' differences and 'within batch' consistency may provide the forensic scientist with the means to discriminate between tape rolls even if they come from the same product line.

## Introduction

Pressure sensitive adhesive (PSA) tape<sup>1</sup> may be associated with criminal activities,<sup>2</sup> e.g., packaging of drugs<sup>3,4</sup> and violent assault.<sup>5</sup> Forensic investigation often requires that a sample found with a suspect be compared with evidence retrieved from a crime scene. Hence techniques capable of demonstrating differences, if any, between two samples are relevant. Techniques used for analysing other polymer products, e.g., plastic films and rubbish bags, can be applied to PSA tape. A combination of physical examination (fit of cut or torn edges,<sup>6</sup> weight per unit area, thickness, optical properties<sup>3</sup> and markings<sup>7,8</sup>) and chemical methods (UV/VIS,<sup>3,9</sup> FTIR,<sup>3,9-14</sup> pyrolysis GC-MS,<sup>10,13,15</sup> XRF<sup>16,17</sup> and NAA<sup>18</sup>) are used. Maynard *et al.*<sup>2</sup> commented that, in Australia, the PSA tapes most commonly encountered in investigations are packaging tapes and clear sticky tapes. In The Netherlands it is brown PSA packaging tape that is encountered most commonly. By using first FT-IR and then EDXRF it was found to be possible to discriminate between different brands of such tape.<sup>19</sup> Furthermore, for one particular brand, EDXRF data indicated differences between some, but not all, of the tape rolls studied. Analysis of the trace elements appears to be a promising route for discriminating between rolls of brown PSA packaging tape. Unfortunately XRF lacks sensitivity for this task. In this work we describe a suitable method for digesting brown PSA packaging tape and the application of ICP-MS to the measurement of trace elements in the glue. This enabled us to discriminate between different tape rolls within a brand, for all three brands studied here. This was not possible with FT-IR and EDXRF alone.

## Experimental

### Reagents

Nitric acid (65% m/m), hydrogen peroxide (30% v/v), hydrochloric acid (37% m/m) and hydrofluoric acid (40% m/m), all Suprapur grade, were obtained from Merck (Germany). De-ionized water (Milli-Q, Millipore, USA) was used throughout. Multi-element standards were obtained from PerkinElmer (The Netherlands) and CPI International (The Netherlands). A Rh standard solution was also obtained from CPI

International for use as an internal standard. Working standards (2, 10 and 50 ng mL<sup>-1</sup>) were prepared fresh on a daily basis by serial dilution.

### Samples

Rolls of brown PSA packaging tape [TESA brand (Type 4024) from Gamma, V&D proprietary brand and Blokker proprietary brand] were purchased at different times from separate shops belonging to three different chain stores in The Netherlands. These chain stores were chosen because they each have many outlets throughout The Netherlands. This means our feasibility study was based on typical tape samples taken only from very common Dutch sources. Additional tape rolls were also obtained directly from the manufacturer of TESA tape.

### Sample preparation

Samples were manipulated in a class 100 laminar flow bench (Interflow, Wieringerwerf, The Netherlands). Powder-free vinyl gloves were worn and changed frequently during handling. Tape rolls were first unwound several turns to access the inner tape. The unwound tape was laid adhesive side upward on the inside rear surface of an opened plastic folder. The plastic folder had three pre-cut holes in the upper side that served as a template defining the regions to be sampled. After the plastic folder had been closed on top of the adhesive side three regions of the tape remained exposed, each region being approximately 10 cm<sup>2</sup> in area.† A 2 mm strip along the sides of each exposed sample area was removed (using a ceramic knife, Fisher

†Concerning real casework, this methodology can be applied when two or more layers of PSA tape partially covering each other are available. An example could be violent crime, where PSA tape is wrapped around a victim's hands or feet to bind them together. Providing the tape is wound around at least twice, such that the second winding at least partially covers the first winding, there will be some uncontaminated tape available for analysis. In such a scenario 10 cm<sup>2</sup> might be available, but the sensitivity of ICP-MS means that smaller samples could also be analysed. Drugs enclosed in boxes could also be an application. To prevent easy detection by sniffer dogs, such packages tend to be well wrapped, i.e., several layers of packaging tape. It is not necessary to analyse the layer originally stuck to the paper/cardboard when there are several layers of tape one on top of another.

**Table 1** Conditions for microwave digestion

	Power/W	Time/min
Step 1	700	12
Step 2	1000	20
Step 3	0	35

Scientific, The Netherlands) to preclude contamination from the exposed edge of the tape rolls. The exposed areas were either cut out (whole tape digestions) or the glue layer was scraped off the backing layer (glue and backing layers digested separately). The latter was accomplished by placing a minimal volume of methanol (HPLC Grade, Rathbone, UK) dropwise onto the glue layer. Methanol proved the most suitable solvent because it dried slowly enough to allow the glue to be scraped off and because it was compatible with both acrylic- and rubber-based glues. The temporarily mobilized glue was scraped off with two PTFE spatulas (Fisher Scientific, The Netherlands). The glue was kneaded between the spatulas to promote drying of excess methanol and agglomeration of the glue. The glue was then left in the laminar flow bench to dry (30 min) at ambient temperature.

### Sample digestion

A closed vessel microwave digestion unit (Multiwave, Anton Paar, Austria) was used to achieve sample dissolution. Samples (*ca.* 50 mg for glue or backing layer, 100 mg for whole tape) were placed inside cleaned quartz vessels (capable of withstanding 75 bar and 300 °C) containing 5 mL concentrated nitric acid, 3 mL hydrogen peroxide (30% v/v) and 2 mL water. Table 1 shows the power settings and irradiation times employed. The digested samples (14 mL in total, including rinsings) were stored in 15 mL polypropylene screw capped tubes (Sarstedt, Germany) prior to analysis. After centrifugation (2500 rev min<sup>-1</sup> for 15 min), aliquots (10 mL for glue or backing layer digests, 5 mL for whole tape digests) were pipetted into acid-cleaned polypropylene volumetric flasks and diluted to 100 mL with water prior to ICP-MS analysis. Four samples of each tape roll were taken. For nine tape rolls, plus a procedural blank and control sample in each carousel, this meant nine digestion series. A randomized scheme was selected where each sample was digested in duplicate on two days.

### ICP-MS instrumentation

Two double focussing magnetic sector ICP-MS instruments (Element, Finnigan, Germany) were used. Model 1 was operated with a water-cooled (5 °C) Scott-type double pass quartz spray chamber and a concentric nebulizer (TR-3, Meinhard, USA, or Conical, Glass Expansion, Switzerland). Model 2 was equipped with an inert sample introduction system comprising MCN 100 micro-concentric nebulizer (Cetac, USA), acid resistant torch and spray chamber (Finnigan, Germany), and was operated with the guard electrode. A peristaltic pump was used for sample uptake for both models. Software versions 1.7, 2.0 and 2.1 were used, but in all cases the spectrometers were operated in the electric scanning mode ( $\pm 15\%$  nominal magnet mass) with the factory default magnet high and low jumps. Instrumental operating conditions are given in Table 2.

## Results and discussion

### Sample preparation and digestion

A description of the structure and composition of PSA tape is given elsewhere.<sup>1,20,21</sup> For the purposes of this discussion it is sufficient to consider such tape as consisting of two layers, namely the pressure sensitive adhesive layer (the glue) and a

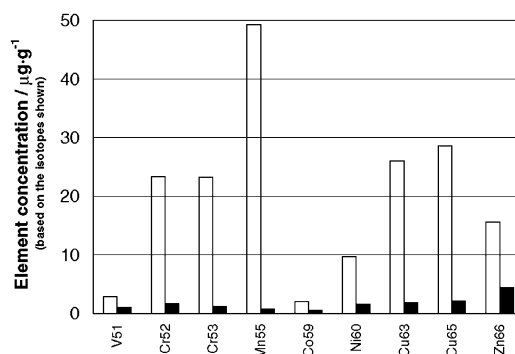
**Table 2** Instrumental conditions and measurement parameters for the Finnigan MAT Element ICP-MS

Forward power	1400 W
Reflected power	< 5 W
Gas flow rates	
Plasma	14 L min <sup>-1</sup>
Auxiliary	0.9 L min <sup>-1</sup>
Nebulizer	1 L min <sup>-1</sup>
Mass window	80%
Search window	150%
Integration window	80%
Runs/passess	3/3
Samples/peak	20
Sample time	0.025–0.15 s
Acquisition mode	E-scan
Internal standard	Rh (10 ng g <sup>-1</sup> in solutions analysed)
Selected isotopes	<sup>51</sup> V, <sup>52</sup> Cr, <sup>53</sup> Cr, <sup>55</sup> Mn, <sup>59</sup> Co, <sup>60</sup> Ni, <sup>63</sup> Cu, <sup>65</sup> Cu, <sup>66</sup> Zn, <sup>103</sup> Rh
Sample uptake rate	Model 1 ~ 1 ml min <sup>-1</sup> , Model 2 0.1 ml min <sup>-1</sup>
Wash/rinsing time	3 min
Take up time	2 min

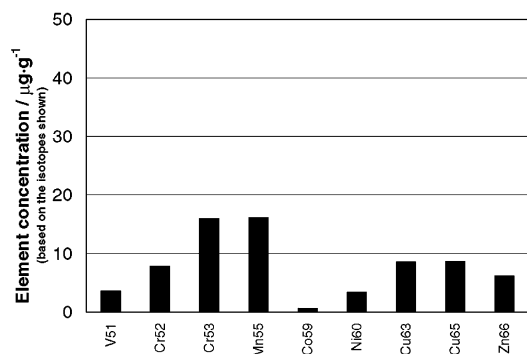
carrier, or backing, layer usually made of bi-axially orientated polypropylene (BOPP). For the tape rolls studied here, the glue was either based on natural rubber or a synthetic acrylic based polymer.

Fig. 1 reveals that, for this type of adhesive tape roll, the vast majority of the transition metal elements present can be found in the glue layer, not the carrier layer. (The backing layer has little forensic significance because only a handful of manufacturers supply all the BOPP used in Europe and being so widespread the backing layer offers little potential for discriminating between brands or rolls.) Since the analytical signal originates essentially from only the glue layer, the choice of whether to separate the layers, and digest them individually, or to leave the tape intact and digest the whole sample might appear irrelevant. Whilst digesting the whole tape is certainly more convenient in terms of sample handling, the following issues dictated that the layers first be separated.

To break down the whole tape required the inclusion of hydrochloric acid amongst the digestion reagents (even in quartz vessels at 280 °C and 55 bar with nitric acid (7 mL) and hydrogen peroxide (3 mL), undigested tape is left stuck to the walls). When the two layers were digested individually (either in plastic or quartz vessels) no hydrochloric acid was necessary (providing the temperature and pressure exceeded 240 °C and 30 bar). Furthermore, for digestion of whole tape samples (*i.e.*, hydrochloric acid included), the concentrations were found to be generally lower than for glue samples digested separately without hydrochloric acid (*cf.*, manganese concentrations in



**Fig. 1** Elemental concentrations within TESA adhesive packaging tape (acrylic based glue). ICP-MS measurements made in medium resolution. All data is procedural blank corrected. Sample masses were ~0.06 g and ~0.05 g for carrier and glue layers, respectively. Digestion reagents were nitric acid (5 mL) and hydrogen peroxide (3 mL). For microwave conditions, see Table 1. Legend: ■ = concentration in carrier layer; □ = concentration in glue layer.



**Fig. 2** Elemental concentrations in TESA adhesive packaging tape (acrylic based glue) digested whole. ICP-MS measurements made in medium resolution. All data was procedural blank corrected. Sample masses were  $\sim 0.11$  g. Digestion reagents were nitric acid (8 mL), hydrochloric acid (2 mL) and hydrogen peroxide (2 mL). For microwave conditions, see Table 1.

Figs. 1 and 2) even when the greater mass of the whole tape was accounted for.

In medium resolution mode it should be possible to resolve the polyatomic interferences (*e.g.*,  $\text{ClO}^+$  on  $^{51}\text{V}$  and  $^{53}\text{Cr}$ ) arising from hydrochloric acid present in the digestion medium. When chromium was determined in whole-tape digests (hydrochloric acid present) using the medium resolution setting, the values based on  $^{52}\text{Cr}$  and  $^{53}\text{Cr}$  did not agree (see Fig. 2). In the absence of hydrochloric acid (*i.e.*, layers separated and digested individually), the values based on  $^{52}\text{Cr}$  and  $^{53}\text{Cr}$  did agree (*cf.*, Figs. 1 and 2). This suggested that the inclusion of hydrochloric acid for whole-tape digestion generated interferences other than the well-known  $\text{ClO}^+$  polyatomic species. Rather than identify and resolve these interferences we concluded that it was preferable to omit hydrochloric acid completely. This required that the layers be separated prior to digestion. Measurements were still made in the medium resolution mode, however, because the final dilutions of the sample digests contained sufficient nitric acid to generate an interference ( $^{40}\text{Ar}^{15}\text{N}^+$ ) on  $^{55}\text{Mn}$ .

The microwave irradiation time and power were optimised to achieve a steady rise in temperature and pressure over 10 min, whereupon the maximum pressure was attained. For these samples (organic matrix), operation of the magnetron was regulated with respect to the pressure, *i.e.*, the maximum pressure was reached before the maximum temperature. These steady state conditions were maintained for a further 20 min.

Quartz digestion vessels were preferred to Teflon vessels because lower procedural blanks were obtained. Furthermore, higher operating pressures and temperatures could be used. Early attempts at digesting the glue samples had shown that, when digestion conditions are inadequate (too low a pressure, too low a temperature), a reddish brown suspension can be the result. EDXRF analysis of one such suspension (after centrifuging and decanting of the supernatant) revealed that titanium and iron (as much as several percent) were the main inorganic components. However, quartz vessels prohibit the use of hydrofluoric acid as a digestion reagent. Without hydrofluoric acid (for both whole-tape and separated layer digests) a white precipitate was observed after digestion, *i.e.*, the sample was not dissolved completely. Given the white colour of the precipitate, the strongly oxidising conditions, the fact that titanium dioxide is ubiquitous in manufactured products and the EDXRF analysis, we considered this precipitate to be titanium dioxide. By centrifuging the digests we aimed to separate the precipitate, thereby preventing blockage of the nebulizer during aspiration of the diluted digests. If hydrofluoric acid were to be included amongst the digestion reagents then, given the amount of titanium present in the glue,  $\text{MO}^+$  interferences would be anticipated (*e.g.*,  $^{48}\text{Ti}^{16}\text{O}$  on  $^{64}\text{Zn}$

and  $^{50}\text{Ti}^{16}\text{O}^1\text{H}$  on  $^{66}\text{Zn}$ ). Additionally, a quartz spray chamber might not be suitable, depending on the hydrofluoric acid concentration. Of course a precipitate could bias (negatively) our results, *e.g.*, *via* adsorption of the elements we are trying to measure. To assess this possibility, the manganese concentrations in samples digested with and without hydrofluoric acid were determined by means of ICP-AES [only manganese was present at a sufficiently high concentration to be measurable with the radial ICP-AES available (Optima 3000, PerkinElmer, USA)]. The manganese concentration was found to be the same (within the limits of experimental error) for both types of sample digest. It was concluded that the precipitate did not compromise the digestion procedure.

### Quantification

Determining the mass of glue scraped off the carrier layer was difficult because the solvent caused the glue to swell. Attempts to dry the glue to constant mass were not successful. The mass was determined indirectly. The tape was first weighed intact and then, after removal of the glue, the carrier layer was weighed. The difference in mass was attributed to the glue. With practice it was possible to scrape the glue off with a good reproducibility. For example, tape from one brand was found to be  $55 \pm 3\%$  glue and  $45 \pm 3\%$  carrier on a w/w % basis. Of course this does not take into account the possibility that the carrier layer also absorbs solvent, but any methanol absorption by the polypropylene carrier layer should be negligible, certainly in comparison to the observed swelling of the glue. Any absorption of solvent by the carrier would only lead to lower values for the glue masses (given the indirect determination) and would translate into higher reported concentrations in the dry glue. Since we could not assess how relevant this potential problem was, producing accurate fully quantitative data for this sample matrix was a challenging task.

Despite concern over gravimetric accuracy and practical difficulties of weighing sticky samples, several fully quantitative analyses of tapes were made (all quantities were calculated by ordinary least squares regression of the linear calibration function obtained from external standards containing Rh ( $10 \text{ ng mL}^{-1}$  in nebulized solutions) as an internal standard). Nevertheless, this tedious sample preparation was not suitable for a routine method. From a forensic point of view the aim is to compare tapes on the basis of their elemental compositions. To this end, knowing the ratio of two elements is more interesting than knowing their absolute concentrations. Of course, accurately determining their absolute concentrations in the dry glue would give the most accurate value for this ratio, but this is not strictly necessary. An alternative is to scrape glue from a fixed surface area on all samples (experimental observations showed this approach gave samples in the range  $50 \pm 5 \text{ mg}$ ) and to digest it without weighing. This saved time and was sufficient for our purposes. By determining the elemental concentrations in the solution of the digested glue, elemental ratios could be calculated. Since the elements present in the solution of the digested glue came from the glue, these elemental ratios are characteristic of the glue and can be used to compare different tapes. We found this approach to be effective and efficient.

Whilst the aim was to use elemental ratios to compare different samples, the digestion and measurement procedure must yield accurate results for the concentrations used as numerator and denominator in such ratios. The authors are unaware of any adhesive tape reference material certified for elemental concentrations. The accuracy of the digestion and measurement procedure was assessed by analysing the certified reference material (CRM) BCR-680, which is based on a polyethylene matrix. However, of the seven first row transition metals we measured in these tape samples, Cr is the only one that is certified in this CRM (see Table 3). This situation is

**Table 3** Determination of heavy metals in CRM BCR-680 using digestion conditions and measurement parameters given in Table 1 and Table 2, respectively. Results are expressed as mg kg<sup>-1</sup>

Element	Concentration	
	Found <sup>a</sup>	Certified <sup>b</sup>
S	n.d. <sup>c</sup>	0.67·10 <sup>3</sup> ± 0.07·10 <sup>3</sup>
Cl	n.d. <sup>c</sup>	810 ± 16
Cr	123.9 ± 1.0	114.6 ± 2.6
As	n.d. <sup>c</sup>	30.9 ± 0.7
Br	n.d. <sup>c</sup>	808 ± 19
Cd	144.4 ± 3.0	140.8 ± 2.5
Hg	n.d. <sup>c</sup>	25.3 ± 1.0
Pb	106.1 ± 0.9	107.6 ± 2.8

<sup>a</sup>Mean value ± standard deviation ( $n = 4$  independent digestions).  
<sup>b</sup>BCR-680 certificate of analysis. <sup>c</sup>n.d. not determined in this work.

admittedly far from ideal. To ensure that the methodology worked for metallic elements other than Cr present in a polymer matrix, the concentrations of Cd and Pb in this CRM were also determined. The concentrations of the more volatile elements, As and Hg, were not determined because we anticipated losses under the microwave digestion conditions applied. The digestion carousel also included a procedural blank and this was used to correct the data of the CRM digests. Good agreement was found for Cd and Pb, whilst the value for Cr was slightly higher than the certified value (see Table 3). The BCR-680 certificate of analysis recommends 500 mg as the minimal sample intake, in order to allow for any heterogeneity of these elements within the polymer matrix. We digested 100 mg samples of BCR-680 because the tape sample intake masses were always ~50 mg for glue samples and ~100 mg for whole tape samples. The slightly higher Cr value could arise from this difference in intake mass.

All the tapes studied contained measurable amounts of the elements, V, Cr, Mn, Ni, Co, Cu and Zn, in the glue layer. Fig. 1 shows the concentrations found in an acrylic-based glue. For the rubber-based glue (Blokker brand tapes), the Zn concentration is markedly higher than in the acrylic-based glues (data not shown). Among these elements, V and Co are present at the lowest concentrations. One vessel in every digestion carousel was a procedural blank digestion (acid but no tape sample). These procedural blank digestions were treated and measured in the same way as the tape sample digests. The elemental concentrations in these blank digestions were very consistent, so an average procedural blank concentration was calculated for each element. These concentrations (see Table 4) were used to correct the tape sample data for the procedural contribution. For V and Co, the procedural blank contribution was an appreciable portion of the V and Co signals of the diluted sample solutions introduced into the ICP-MS. For the other elements the procedural blank contribution was inconsequential and the consistency of the procedural blank concentration meant that these elements were well corrected. This might suggest that V and Co are less reliable discriminators than the other elements. Nevertheless, the ratio <sup>55</sup>Mn/<sup>59</sup>Co was found to have a similar reproducibility ( $s_R$ ) to, for example, <sup>52</sup>Cr/<sup>55</sup>Mn (see Table 5).

A sample of one roll (referred to as the “control tape”) was included in every digestion series. This enabled us to monitor our results for consistency of digestion (on the assumption that there is no variation along the length of this ‘control tape’). A

**Table 4** Concentrations in procedural blank digestions. Results are expressed as µg L<sup>-1</sup>

V	Cr	Mn	Co	Ni	Cu	Zn
0.209	0.220	0.205	0.278	0.311	0.305	0.099

**Table 5** Repeatability and reproducibility data for example element concentration ratios (based on isotopes shown) calculated according to the appropriate equations in ISO 5725-2:1994

	Ratio			
	<sup>52</sup> Cr/ <sup>55</sup> Mn	<sup>60</sup> Ni/ <sup>63</sup> Cu	<sup>51</sup> V/ <sup>52</sup> Cr	<sup>55</sup> Mn/ <sup>59</sup> Co
Reproducibility ( $s_R$ )	3.6%	2.1%	2.0%	3.3%
TESA repeatability ( $s_R$ )	2.8%	2.4%	1.6%	2.2%
V & D repeatability ( $s_R$ )	2.1%	2.6%	2.2%	2.1%
Blokker repeatability ( $s_R$ )	3.8%	9.4%	6.4%	4.6%

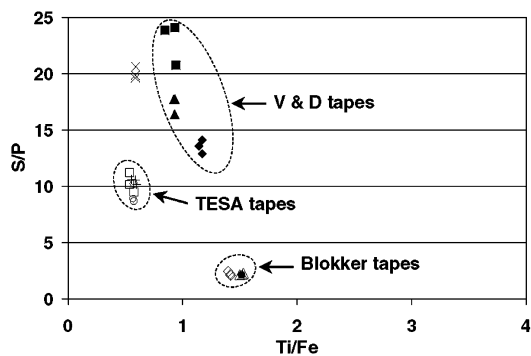
total of 11 independent digestions of the control tape roll were carried out over a period, from start to finish, of 4 months. Furthermore, different analysts performed the digestions and two models of the Element ICP-MS were used. The samples themselves were measured over a period, from start to finish, of 6 months [the samples were not necessarily measured immediately, but were stored (see sample digestion), thus accounting for the difference between 4 and 6 months]. Despite the potential for variation, the data points for this ‘control sample’ were always closely grouped (results for Cr, Mn, Ni and Cu are shown as an  $x$ - $y$  plot in Fig. 7, but the observation also applies to other isotopes measured irrespective of how the data is presented graphically). The sample tape rolls were not subjected to as much potential for variation as the ‘control sample’ because the sample tape rolls were only digested twice in two carousels (giving 2 pairs of independently digested samples for each tape roll). However, the spread in their data points was comparable (sometimes slightly greater, sometimes smaller) to the ‘control sample’. This showed that the method was reproducible in the long term. Furthermore, because the ‘control sample’ was sampled *de facto* over the majority of its length, and yet exhibited comparable variation to tape rolls that were sampled over smaller regions, we can infer that for this roll there was no measurable variation in concentrations along the roll.

The repeatability ( $s_R$ ) (see Table 5) was calculated from all the duplicate digestion data of each tape brand. The repeatability for TESA and V&D tapes was found to be similar. However, the repeatability of Blokker tapes was larger. This is an indication that the Blokker tapes are more heterogeneous with respect to these elements than the TESA and V&D tapes. The reproducibility ( $s_R$ ) (see Table 5) was calculated from real sample data, in our case independent digestions of the ‘control tape’.

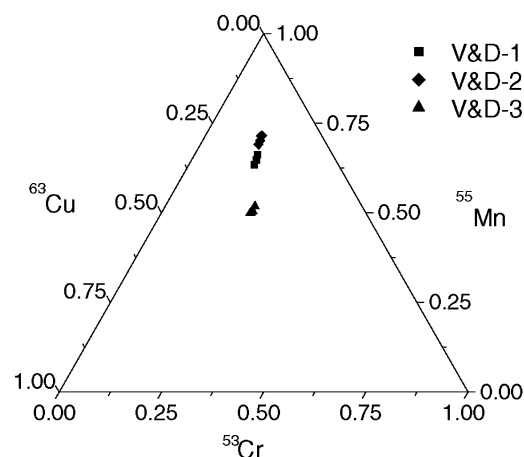
### Comparison of tape samples

By means of FT-IR, the natural rubber PSA tapes (Blokker tapes) were discriminated from the acrylic glue PSA tapes (TESA and V & D tapes).<sup>19</sup> XRF was then used to compare tape rolls within the acrylic group. In fact, as Fig. 3 shows,  $\mu$ -XRF alone gave three groupings, corresponding to the three brands studied here, based on elements present at relatively high concentrations. These techniques are applied first in order to place a tape roll in its correct group (brand). A more difficult task, but potentially more useful in forensic investigations, is to distinguish between the different rolls within the same brand. Fig. 3 shows that such discrimination is possible for the V&D brand but not for the Blokker or TESA brands. The combination of FT-IR and XRF is insufficient for this task.

The sensitivity of ICP-MS permits the determination of elements present at concentrations below the detection limits of  $\mu$ -XRF, which opens up the possibility of using trace elements to discriminate tape rolls. Fig. 4 shows the ICP-MS results for the three different V&D tape rolls (each roll digested twice on 2 days) in the form of a ternary plot (where the concentrations

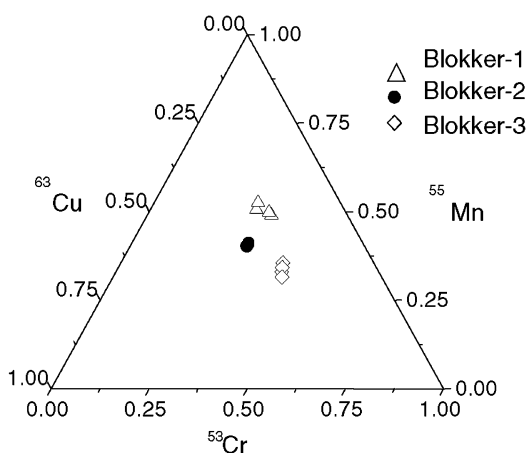


**Fig. 3** Ti/Fe versus S/P signal intensity ratios for 10 different tape rolls (3 different pieces of each roll were irradiated). Tape samples (intact) were pulled taut across the base of conventional XRF sample cups (32 mm diameter) and irradiated under vacuum on the glue side (300  $\mu$ m diameter spot size) using an Eagle II  $\mu$ -XRF spectrometer (EDAX, USA) under the following excitation conditions: 40 kV, 1mA. For sake of clarity the data points of each tape brand are bounded by a dotted line. Nothing should be inferred from the position of these dotted lines. +, TESA-1;  $\square$ , TESA-2;  $\circ$ , TESA-3;  $\times$ , control tape;  $\blacksquare$ , V & D-1;  $\blacklozenge$ , V & D-2;  $\blacktriangle$ , V & D-3;  $\triangle$ , Blokker-1;  $\bullet$ , Blokker-2;  $\diamond$ , Blokker-3.

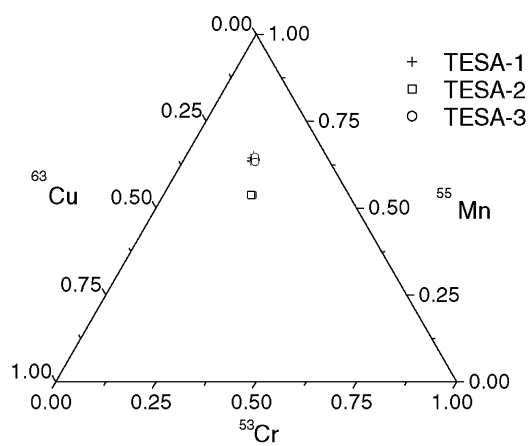


**Fig. 4** Ternary diagram showing inter-element association patterns for glue (acrylic) of three tape rolls purchased from V&D stores.

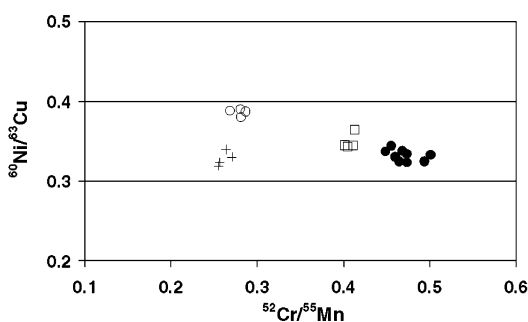
of the three elements, signified by a particular isotope, are normalized to 100%). The use of such plots has already been established.<sup>22-24</sup> On the basis of this ternary plot for Cr, Mn and Cu, these three V&D tape rolls can be distinguished from each other, in agreement with the  $\mu$ -XRF data (Fig. 3).



**Fig. 5** Ternary diagram showing inter-element association patterns for glue (based on natural rubber) of three tape rolls from Blokker stores.



**Fig. 6** Ternary diagram showing inter-element association patterns for glue (acrylic) of three tape rolls (TESA brand) purchased from Gamma stores.



**Fig. 7** Cr/Mn versus Ni/Cu elemental concentration ratios for the three tape rolls referred to in Fig. 6. Element concentrations were calculated based upon measurements of the  $^{52}\text{Cr}$ ,  $^{55}\text{Mn}$ ,  $^{60}\text{Ni}$  and  $^{63}\text{Cu}$  isotopes.  $\bullet$ , Control tape; +, TESA-1;  $\square$ , TESA-2;  $\circ$ , TESA-3.

An analogous ternary plot (Fig. 5) for the three different Blokker tape rolls (each roll digested twice on two days) shows that they can all be distinguished from each other. The reproducibility data (Table 5) indicate that the Blokker tapes are more heterogeneous than the V&D tapes and TESA tapes. Nevertheless, the clustering of the Blokker groups was acceptable.

An analogous ternary plot (Fig. 6) for three different TESA brand rolls (each roll digested twice on 2 days), however, yielded incomplete discrimination.

Yet by combining data from four elements (Fig. 7) these TESA rolls can be distinguished from each other.

#### Comparison of two production batches

PSA tapes typically have no obvious identification marks such as printed lot or production reference numbers. This was also true for the tape samples studied in this work. It is, therefore, possible that, for each brand, we unwittingly analysed rolls from the same production batch. Therefore, rolls from two batches were obtained directly from the manufacturer of TESA with the aim of comparing both between- and within batch samples. These rolls were removed directly from the production line and were from two distinct batches.

Two rolls (referred to as Roll 1 and Roll 2) were chosen randomly from each batch (referred to as Batch 1 and Batch 2) and were sampled at five positions along the roll (referred to as position 1-5 along tape roll). This yielded 20 samples in total (2 rolls  $\times$  2 batches  $\times$  5 positions along a tape roll = 20). These 20 samples were digested in a structurally randomised order (see Table 6) on different days by one analyst (thereby removing the operator as a source of variation) and were

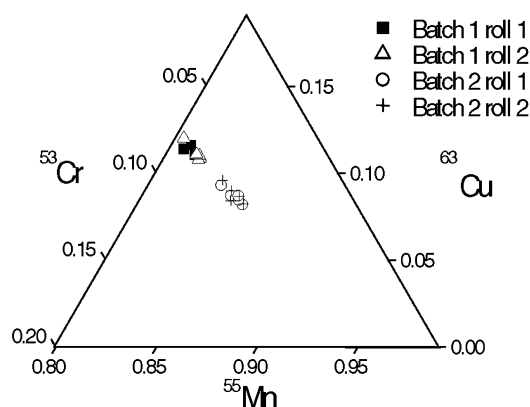
**Table 6** Digestion scheme for double multivariate analysis of variance with repeated measures and nested factors

Digestion	Position along tape roll	Batch	Roll	Position in carousel
1	1	1	1	1
	2	1	2	2
	5	1	2	3
	4	2	2	4
2	3	2	1	5
	3	1	1	1
	5	1	1	2
	4	1	2	3
3	2	2	1	4
	1	2	2	5
	2	1	1	1
	3	1	2	2
4	1	2	1	3
	4	2	1	4
	5	2	2	5
	4	1	1	1
5	1	1	2	2
	5	2	1	3
	2	2	2	4
	3	2	2	5

analysed in one measurement run (*i.e.*, under repeatability conditions to remove day to day measurement variation).

Each digestion carousel contained a procedural blank (acid but no sample). Given that the carousel has 6 positions, only 5 positions are available to accommodate samples. At best, only two carousels of samples can be prepared and digested in one working day. Since not all samples can be digested in one carousel, the digestion process is a source of variation that we cannot eliminate. Clearly the two different batches are also a source of variation; there might also be variation between different rolls within the same batch and variation within one roll along the length of the roll. Together these constitute four potential sources of variation. Given the 5 carousel positions available, 20 is the minimum number of samples required in order to cope with four potential sources of variation. The numbering order in the digestion scheme means that the sample scraped from the beginning of Roll 1 of Batch 1 is placed in vessel 1 of the first digestion carousel, and so on. This scheme made it possible to separate any variation due to the digestion from the variation between the 2 batches and within the 2 batches. The rolls were purposely unwound almost completely to permit samples to be taken from the entire roll. By scraping off glue from points along the entire roll any variation in homogeneity along a roll would become apparent as within roll variation. The results are depicted in Fig. 8.

Data analysis (double multivariate analysis of variance with



**Fig. 8** Ternary diagram showing inter-element association patterns for glue of two different batches (TESA brand, obtained directly from the manufacturer).

repeated measures and nested factors) showed no significant difference within batches but did show a statistically significant difference between batches (Hotellings' test (a kind of *t*-test for multivariate data),  $p = 0.95$ ). A production process that is well controlled can explain this finding. Supporting evidence is also found in Fig. 7, where the data points of the 'control sample' also exhibit good reproducibility despite all the measures taken to provoke variation in the measurement results. A product that is manufactured with a good within batch reproducibility is relevant for forensic purposes because it reduces the chance of any given roll having exactly the same characteristics as a roll from a different batch.

## Conclusion

An analytical methodology, based on microwave digestion of the glue layer and measurement by sector field ICP-MS, to determine trace element concentrations in the glue of brown PSA packaging tapes was developed. Nine tape rolls were analysed and, based upon comparison of the trace element concentrations, all tape rolls could be distinguished from each other, both between different brands and within each brand. This is an improvement over earlier work using EDXRF where this was not possible for all brands. In the case of one brand, for rolls originating from the same product line but from different production batches, it was shown that between production differences are detectable whilst there is no statistically significant difference within rolls from the same production batch. This finding may provide the forensic scientist with a means of discriminating tape rolls even if they come from the same product line. In real forensic cases, the surface area free from contamination (*e.g.*, dirt, blood, tissue, soil, hair, fibres) and hence amenable to this type of analysis, will be smaller than that referred to in this article. Future work will address the need to measure surface areas of 1 cm<sup>2</sup> or less. This could be tackled by miniaturizing the digestion process. LA-ICP-MS is even more attractive because it would save sample preparation time and areas much smaller than 1 cm<sup>2</sup> could be measured.

## Acknowledgement

We would like to thank M. Van Son (Netherlands Metrology Institute, Delft) and W. Zhu (Technical University of Delft, Delft) for the use of their mass spectrometers, and to express our gratitude to M. Sjerps for her expertise in experimental design and multivariate statistical analysis. Further thanks are due to L. Koomen for the  $\mu$ -XRF measurements.

## References

- 1 T. M. Goulding, in *Handbook of Adhesive Technology*, eds. A. Pizzi and K. L. Mittal, Marcel Dekker, New York, 1994, pp. 549–564.
- 2 P. Maynard, K. Gates, C. Roux and C. Lennard, *J. Forensic Sci.*, 2001, **46**, 280–287.
- 3 C. Roux, S. Bull, J. Goulding and C. Lennard, *J. Forensic Sci.*, 2000, **45**, 99–114.
- 4 J. Huttunen, *Platypus Mag.*, (ISSN 0159-1606, Australian Federal Police), 2001, **72**, 16.
- 5 A. Dobney, W. Wiarda, P. de Joode and G. J. Q. van der Peijl, presented at the 53rd Annual Scientific Meeting of the American Academy of Forensic Sciences, Seattle, WA, USA, February 19–24, 2001.
- 6 U. G. von Bremen and L. K. R. Blunt, *J. Forensic Sci.*, 1983, **28**, 644–654.
- 7 D. S. Pierce, *J. Forensic Ident.*, 1990, **40**, 51–59.
- 8 S. Denton, *J. Forensic Sci. Soc.*, 1981, **21**, 259–262.
- 9 R. M. E. Griffin, R. Lewis, J. Bennett, J. Hamill and T. G. Kee, *Sci. Justice*, 1996, **36**, 219–227.
- 10 W. Noble, B. B. Wheals and M. J. Whitehouse, *J. Forensic Sci.*, 1974, **3**, 163–174.
- 11 B. Cleverly, *J. Forensic Sci.*, 1979, **24**, 339–345.

- 12 R. D. Blackledge, in *Applied Polymer Analytical Characterisation*, ed. J. Mitchell, Hanser, Munich, 1987, pp. 413–421.
- 13 A. Pahl, *Kleben Dichten*, 1996, **41**, 28–31.
- 14 R. A. Merrill and E. G. Bartick, *J. Forensic Sci.*, 2000, **45**, 93–98.
- 15 E. R. Williams and T. O. Munson, *J. Forensic Sci.*, 1988, **5**, 1163–1170.
- 16 Y. Nir-El, *J. Forensic Sci.*, 1994, **39**, 758–768.
- 17 T. Ninomoya, S. Nomura, K. Taniguchi and S. Ikeda, *Anal. Sci.*, 1995, **11**, 489–494.
- 18 J. E. Scott, C. M. Hoffman, M. J. Pro and H. L. Schlesinger, *J. AOAC Int.*, 1967, **50**, 371–376.
- 19 A. Dobney, W. Wiarda, P. de Joode and G. J. Q. van der Peijl, in *Problems of Forensic Science*, ed. J. Wojcikiewicz, Institute of Forensic Research Publishers, Cracow, Poland, 2001, vol. XLVII, p. 275–287.
- 20 A. H. Landrock, *Adhesives Technology Handbook*, Noyes Publications, Westwood, NJ, 1985, pp. 174–175.
- 21 K. De Sadhan, in *Handbook of Adhesive Technology*, ed. A. Pizzi and K. L. Mittal, Marcel Dekker, New York, 1994, pp. 315–318.
- 22 R. J. Watling, H. K. Herbert, I. S. Barrow and A. G. Thomas, *Analyst*, 1995, **120**, 1357–1364.
- 23 R. J. Watling, B. F. Lynch and D. Herring, *J. Anal. At. Spectrom.*, 1997, **12**, 195–203.
- 24 R. J. Watling, *J. Anal. At. Spectrom.*, 1998, **13**, 917–926.