Direct analysis of coated and contaminated paper using time-of-flight secondary ion mass spectrometry

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ABSTRACT: This study examines the use of time-of-flight secondary ion mass spectrometry for the direct analysis of two problems common in the paper industry. TOF-SIMS is used to distinguish between paper that gives high-quality print and paper that yields a mottled print. Additionally, an uncoated adhesive label is analyzed to determine the nature of the contaminating species causing spotting. The source of the contamination is also isolated. TOF-SIMS is shown to be capable of giving elemental and molecular information about distribution and relative concentrations of species on paper surfaces.

KEYWORDS: Adhesive papers, impurities, ions, labels, mass spectroscopy, mottle, print quality, spotting, surface properties, uncoated papers.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) has been used extensively for surface analysis in the semiconductor industry. Recently the focus has shifted to other important applications. This study concentrates on solving two problems that occur at different points during paper processing. The first problem to be studied is print mottle on latex coated paper. The second is the determination and isolation of contamination on adhesive labels.

The use of multicolor printing in books, magazines, brochures, and packaging in the graphic arts industry is growing each year. Because of the demand from the graphic arts industry for sharpness and brilliance in printing, a coated paper stock is necessary. Coating with latexes improves printing properties when the mixture is homogeneously applied to a paper surface. However, when inhomogeneity occurs, problems can result in substandard print quality. The most serious problem is mottling of offset print; this is defined as unevenness in print density *(1).* The most common method of evaluating latex film homogeneity is simple visual examination after printing *(2–4).* For example, the Prüfbau backtrap test gives a good indication of a coated paper's predisposition to show print mottle *(5).* Another method that has shown some success is X-ray microanalysis of coated papers; however, this method requires the use of toxic OsO_4 as a tag *(6).*

A second paper processing problem discussed in this study is contamination during in-line manufacturing. Here we look at uncoated adhesive label stock to identify both the nature and distribution of contaminating species. Contamination poses the most significant problem if it is heterogeneously dispersed on the label surface. Uneven dispersion of contaminants on the labels causes discoloration and spotting.

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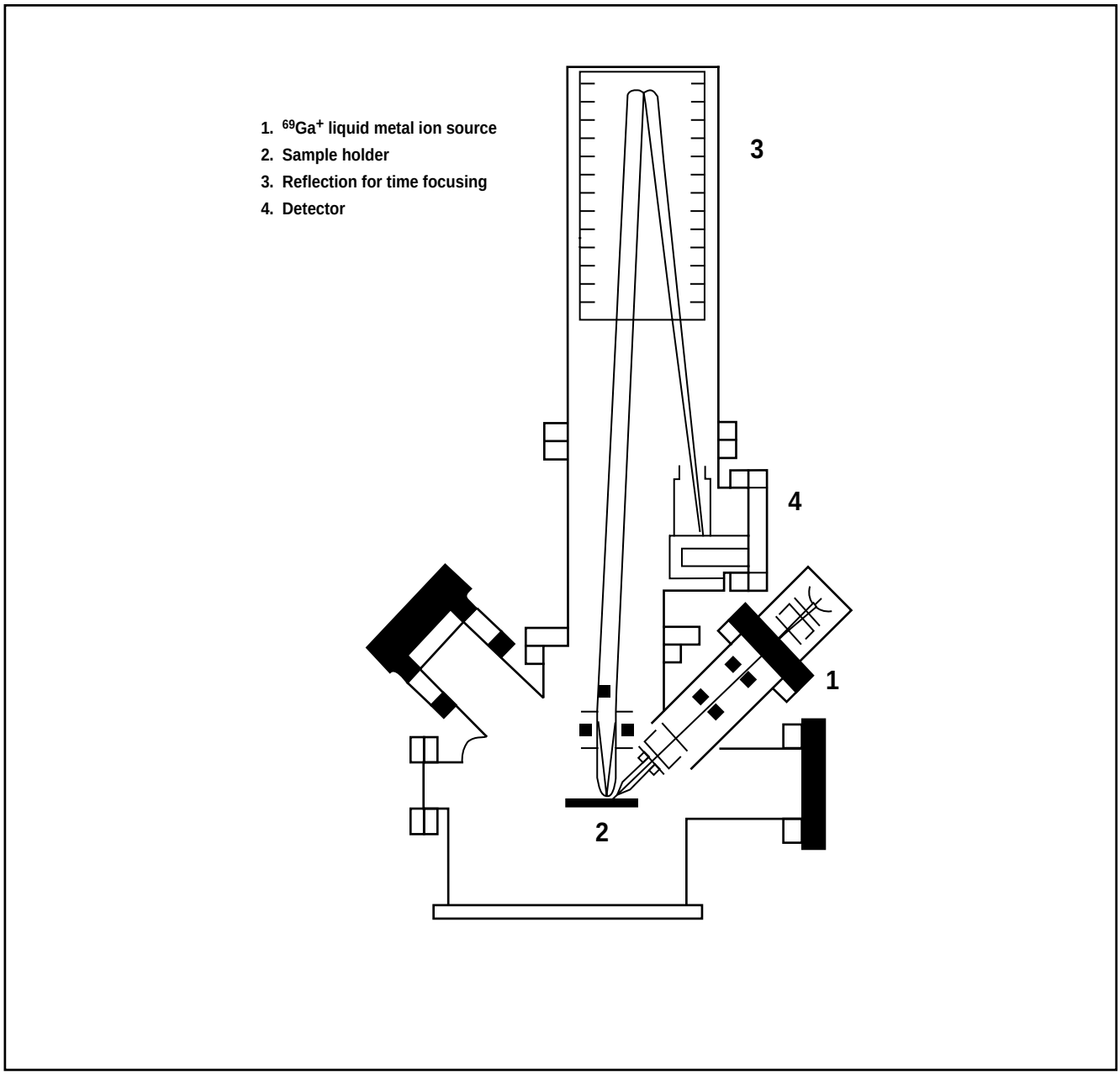
1. Schematic of TOF-SIMS

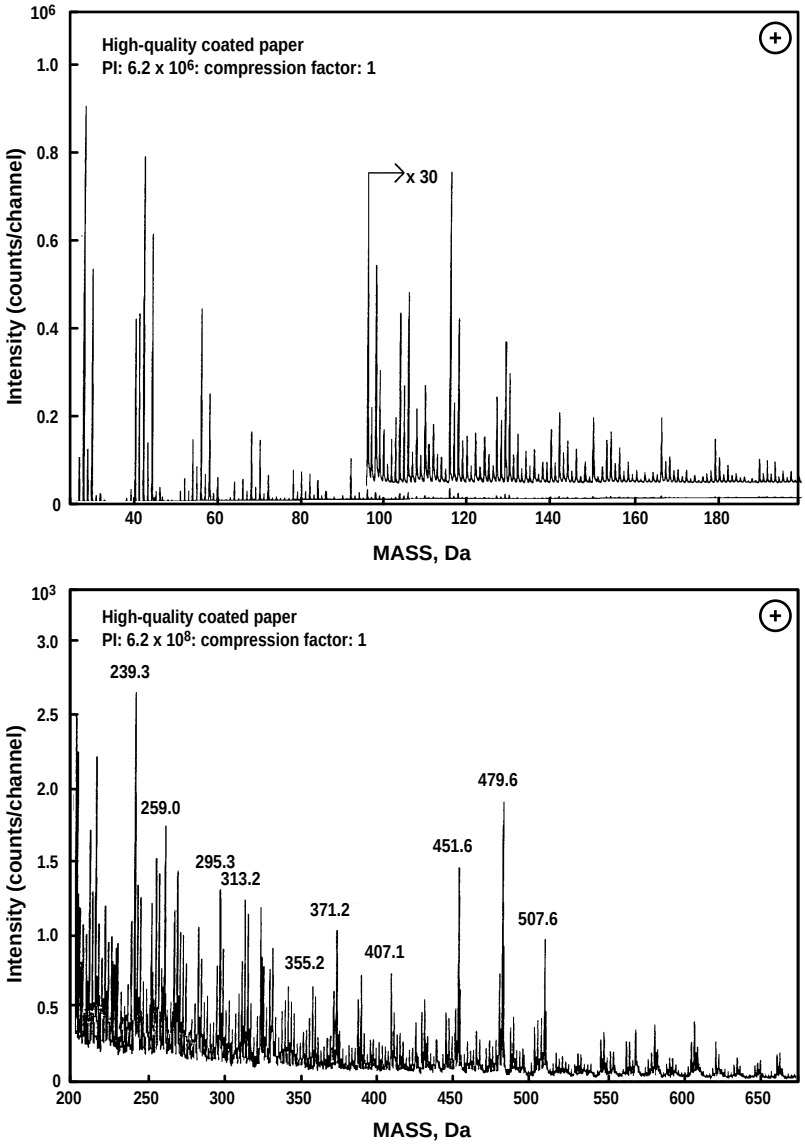


TOF-SIMS uses a primary ion beam to desorb secondary ions, which are mass separated and detected to give a spectrum characteristic of the surface analyzed. TOF-SIMS also allows the analysis of a surface in the static mode. This means that no more than 1% of a monolayer is removed during an experiment; for all practical purposes, the surface remains undamaged *(7)*. The use of TOF-SIMS may offer an analytical method to determine if paper will have mottle when printed. In addition, TOF-SIMS can determine the nature of a contaminating species as well as distributions and relative concentrations on the surface *(8)*. Another advantage of TOF-SIMS for this analysis is that no sample pretreatment is required, and paper can be measured directly.

Experimental

The instrument used to obtain spectra and images was a TOF-SIMS IV developed at the University of Münster and described in detail elsewhere *(9)*. A simple schematic of the instrument is shown in **Fig. 1.** The TOF-SIMS was equipped with a 30-keV liquid metal ion ($^{69}Ga^{+}$) source (LIMS) operating at a current of 1.5 nA. A 40–100 ns pulse length was used to obtain both spectra and im-

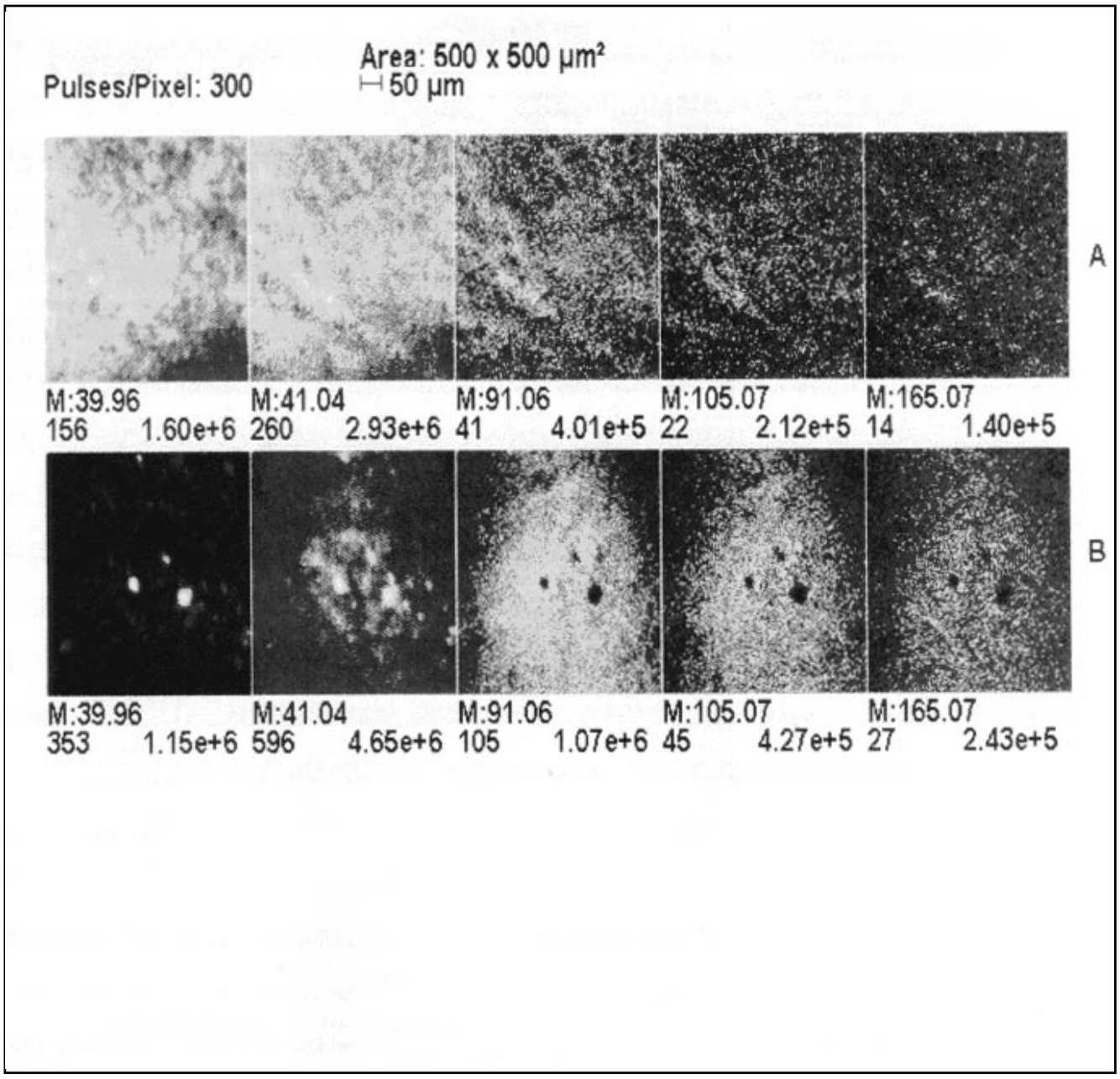
2. TOF-SIMS spectrum of high-quality paper



ages. The primary ion beam was defocused to ca. 1 µm diameter. The spectra and images were accumulated in an ion-counting mode with a time resolution of 472 ps and a total time range of 160 µs. For imaging, a digital raster unit for the pulsed primary beam is set to 256 × 256 or 128 × 128 pixels. For each pixel, the counts are detected in the chosen mass channels and are read out of the time-to-digital (TDC) memory; the counts are written to an image frame buffer in the computer. Charge compensation of the samples was accomplished using a 10-eV electron beam pulsed out of phase with the extraction lens and primary ion beam.

A spectrum was acquired from a region adjacent to an area to be imaged for 100–200 s. From the spectrum, masses of the ions of interest were selected to be imaged. An unlimited number of ions may be imaged simultaneously; however, the data file size is proportional to the number of ions imaged. The time necessary to acquire the data file for ion images is 35–60 min. The color scale appears to the right of each image. The maximum intensity(counts/pixel) in each image is represented by the brightest color on the scale. The numbers under the individual images correspond to the mass of the ion, the

3. TOF-SIMS image of (a) high-quality paper and (b) substandard paper



maximum number of counts/pixel, and the total number of counts/image.

The first analyses consisted of comparing spectra and images from known high-quality and substandard coated papers. The quality of the paper was confirmed by using a backtrap mottle test on a Prüfbau backtrap tester. These papers were coated with a latex/$CaCO_3$ mixture. The latex coating on the paper was a cross-linked styrene-butadiene copolymer. An area of 500 µm^2 was imaged for the coated papers. The second analysis was standard uncoated adhesive label stock that was contaminated during the manufacturing process.

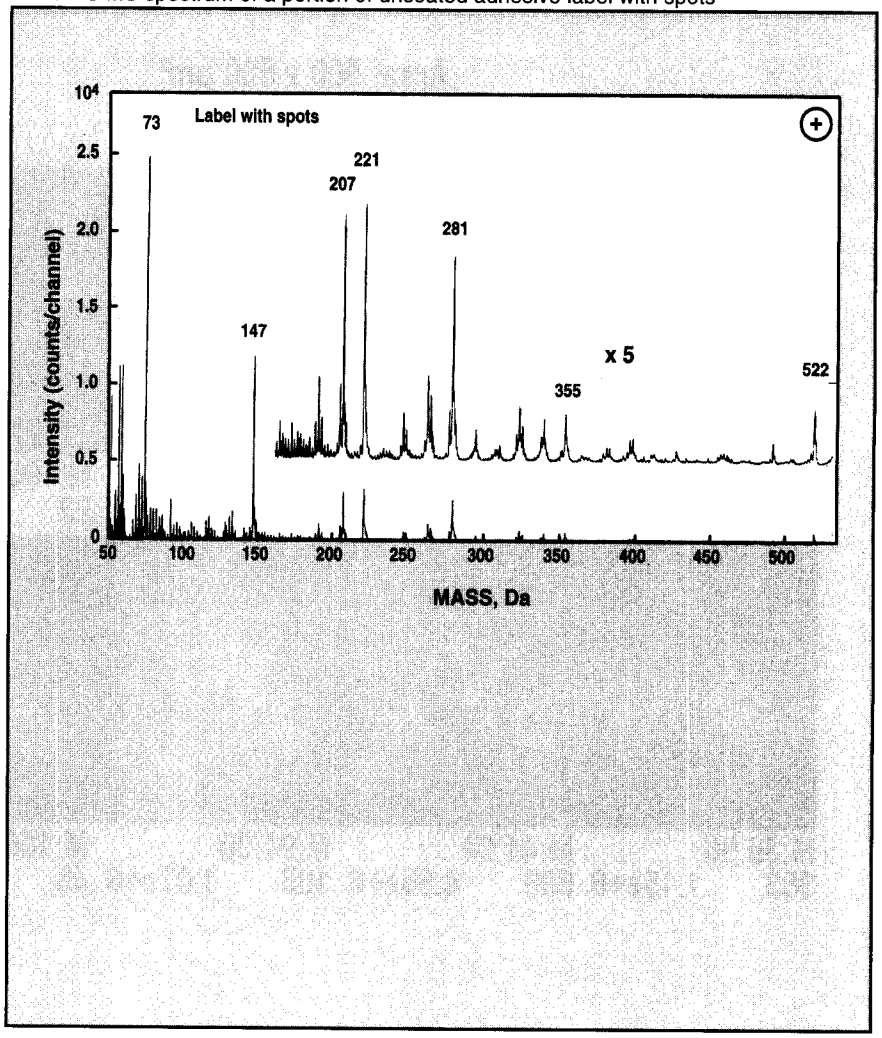
Results and discussion

Coated paper analysis

Figure 2 shows a typical spectrum from the high-quality paper; the spectrum obtained was independent of location. However, spectra obtained from the poor-quality paper showed variability in absolute intensities from spot to spot, indicating an inhomogeneous surface. **Table I**

shows the relative intensities from some of the ions observed using TOF-SIMS. The intensities that are normalized to the $C_7H_7^+$ ion were obtained by acquiring TOF-SIMS spectra from six different points on a sample. Sample-to-sample reproducibility for high-quality paper was within 5% (relative intensity). There is a clear difference in the relative intensity of the Ca^+ ion from spot to spot on the poor-quality paper, indicating inhomogeneity on the surface. Although there were differences in the intensities of ions between the good- and poor-quality paper, there were no extraneous ions present on either paper. **Figure 3(a)** shows the 500-μm² image of a good-quality paper. The masses collected correspond to Ca^+(40 Da), $C_3H_5^+$(41 Da), $C_7H_7^+$(91 Da), $C_8H_9^+$(105 Da), and $C_{13}H_9^+$(165 Da). The images show fairly homogeneous coverage in a 500-μm² area. This is true for all other ions analyzed (not shown) except sodium. The sodium may be segregated in local submonolayer domains, since there is no correlation with the intensities of other atomic and molecular ion images. The $C_7H_7^+$, $C_8H_9^+$, and $C_{13}H_9^+$ ions (91–165 Da) correspond to fragmentation products of the latex. The strong Ca^+ signal arises from the addition of $CaCO_3$ to the coating mixture. **Figure 3(b)** shows the corresponding images of paper that gave a mottled pattern when printed. Note the bright spots for the calcium. These spots are complementary to darker spots found on the images for the hydrocarbon fragment ions from the latex. In addition, there is much less homogeneity in the images from the mottled paper when compared to the good-quality paper. This is especially true in the case of the calcium. The surface distribution of calcium and latex apparently must be fairly homogeneous to ensure satisfactory quality of the coated paper. Although only 500 μm² of paper were imaged, it was indicative (from multiple images) of the quality of the coated paper analyzed.

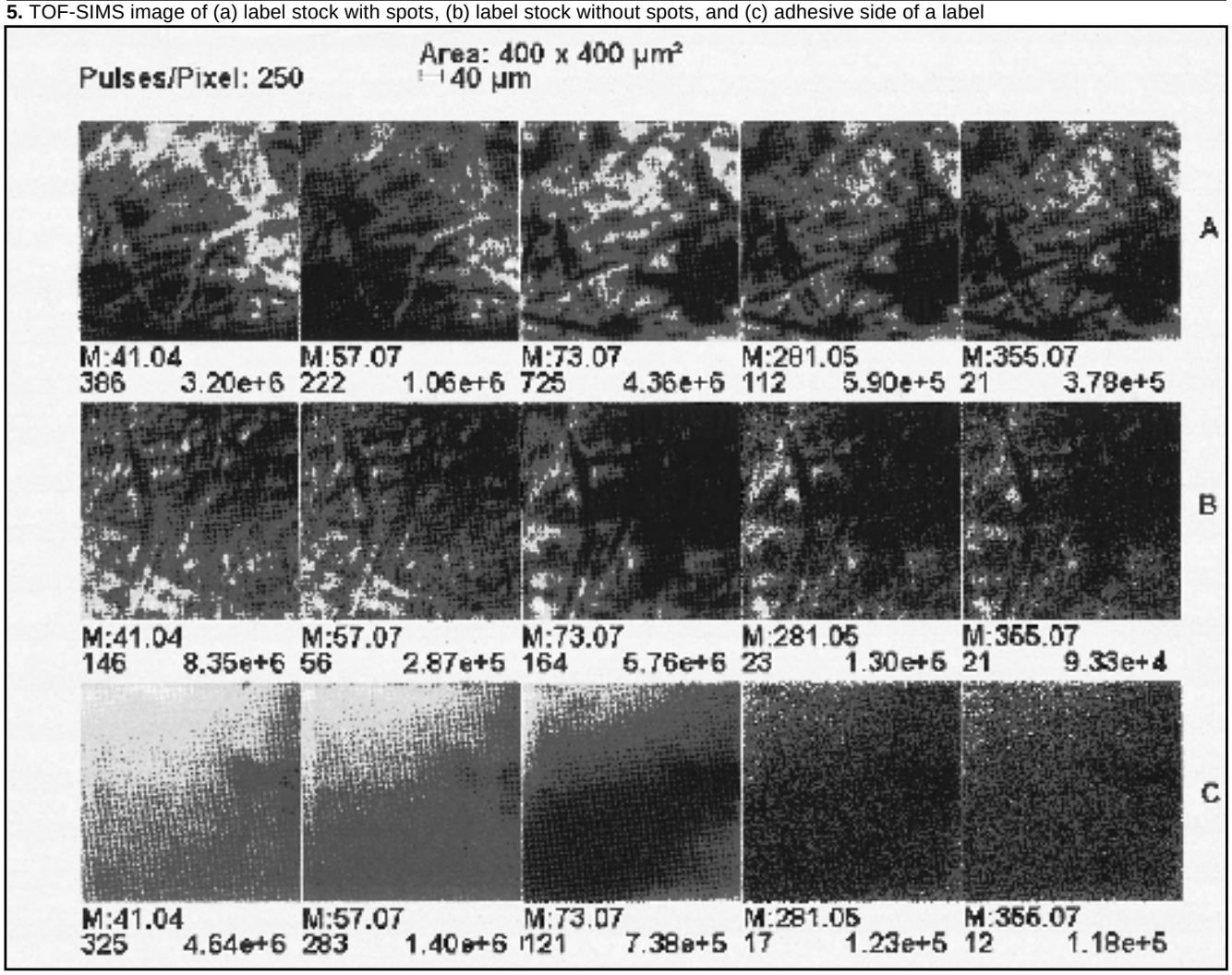
4. TOF-SIMS spectrum of a portion of uncoated adhesive label with spots



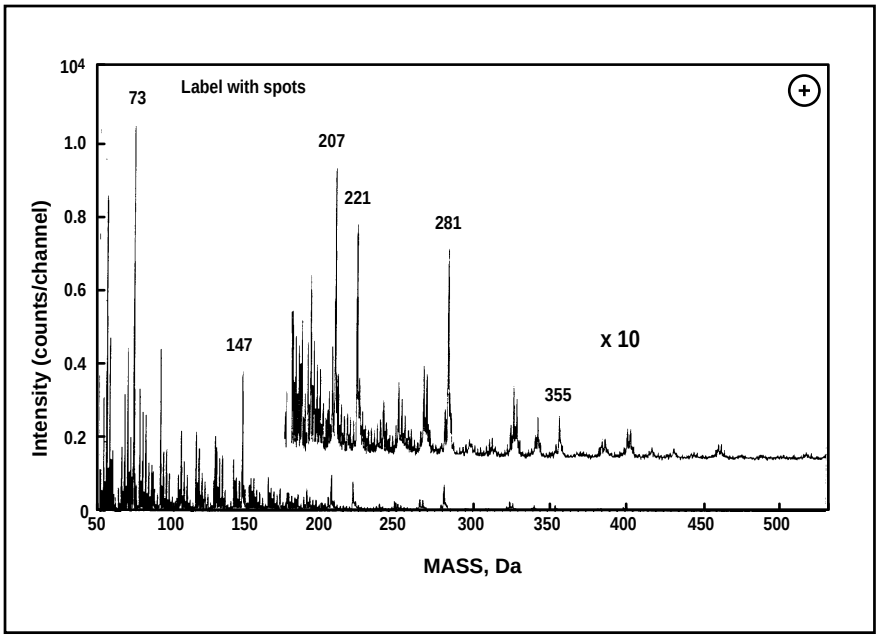
Adhesive label analysis

Figure 4 shows a spectrum obtained from the surface of an adhesive label containing spots. The spectrum shows very high intensities of fragment ions at mass/charge ratios of 73, 147, 207, 221, 281, and 355. This fragmentation pattern is characteristic of polydimethylsiloxanes (PDMS). **Figure 5(a)** shows a 400-μm² image of the top of an adhesive label that has been contaminated; this resulted in spotting during manufacturing. The ions that were monitored include $C_3H_7^+$(41Da), $C_5H_7^+$(91 Da), $C_2H_5OSi^+$(73 Da), $C_7H_{21}O_4Si_4^+$(281 Da), and $C_9H_{27}O_5Si_5^+$(355 Da). The presence of contamination from PDMS is evident from siloxane fragments observed at 73, 147, 221, 281, 369, 355, and 522 Da (Fig. 4). The images show that the concentration of siloxanes is relatively high and the distribution is widespread in the imaged area. **Figure 6** shows a spectrum of a portion of the same adhesive label where spotting is not present. Clearly the fragment ions corresponding to PDMS are also present; however, the relative intensities are significantly lower. Figure 5(b) shows an image of the same adhesive label in an area free of spots. The image shows the presence of siloxane ions (e.g., $C_2H_5OSi^+$, $C_7H_{21}O_4Si_4^+$, and $C_9H_{27}O_5Si_5^+$) as in Fig. 5(a). However, the relative intensities are significantly smaller than on the portion of the label with spots.

5. TOF-SIMS image of (a) label stock with spots, (b) label stock without spots, and (c) adhesive side of a label

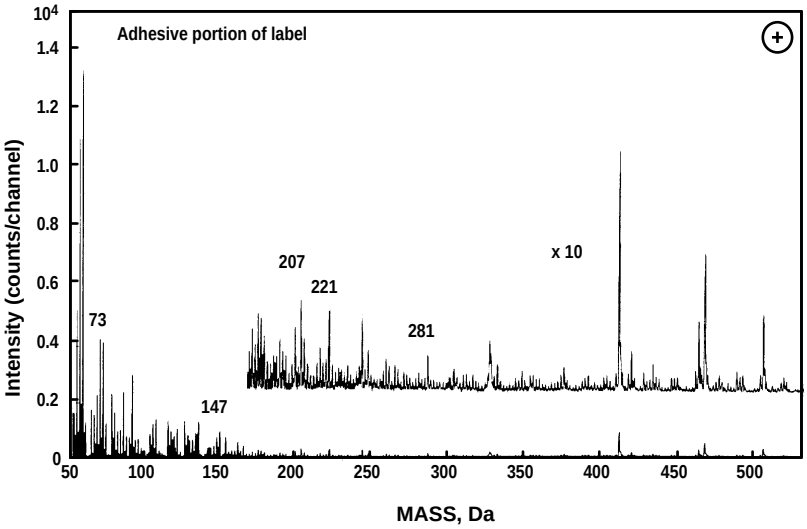


6. TOF-SIMS spectrum of a portion of uncoated adhesive label without spots



The contamination observed may originate from the adhesive material on the back of the label or from the release sheet. **Figure 7** shows the spectrum from a portion of the label with spots and from the adhesive side of the label. Clearly, the concentration of PDMS is substantially lower from the adhesive than it is from the top of the label. Figure 5 (c) shows an image of the adhesive side of the label and supports the conclusion that the contamination did not originate from the adhesive. The source of the contamination, therefore, must be the release sheet, which comes into contact with the top of the label stock as it is rolled or stacked.

7. TOF-SIMS spectrum from the adhesive material on the label



I. Relative intensities of selected ions for high-quality and defective paper

Ion	*Quality paper*	*Defective paper*
Ca^+	301±21	452±93
$C_3H_5^+$	618±32	673±24
$C_4H_9^+$	274±6	290±10
$C_5H_9^+$	152±15	149±9
$C_6H_5^+$	63.3±5.6	65.4±4.8
$C_7H_7^+$	100	100
$C_9H_7^+$	37.4±0.4	38.2±0.8

Conclusions

Two real-world problems from the paper industry were examined using TOF-SIMS. The paper that gave substandard print quality was shown to have surface concentrations of calcium that were not homogeneous. In addition, where the surface concentration of calcium was highest, there was a deficiency in the latex coating on the paper. The TOF-SIMS of the high-quality paper shows fairly uniform distribution of calcium and latex on the surface.

The analysis of contamination on an adhesive label showed high levels of PDMS present. The PDMS was widely distributed over the imaged area on the label with spots and much less so on the label without spots. Furthermore, TOF-SIMS determined that the source of the contamination was not the adhesive material on the label but most likely the release sheet on top of the label.

Analyses of the paper samples were completed with no sample preparation. This work shows that TOF-SIMS can be applied to the direct analysis of important samples other than those found in the semiconductor industry. ■

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