

Paper

Results of Inter-laboratory Tests among SASJ on Accurate Mass Scale Calibration of ToF-SIMS

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(Received : October 3, 2010; Accepted : January 5, 2011)

To evaluate the present errors in the calibration of the mass scale of time-of-flight secondary ion mass spectrometry (ToF-SIMS) in the practical field of Japanese industries, ToF-SIMS Working Group (WG) of Surface Analysis Society of Japan (SASJ) conducted the inter-laboratory studies among 14 instruments in 2007, 2008 and 2009. There was significant scatter over 200 ppm in the relative mass accuracy at the first inter-laboratory test in 2007. Clearly, this is poor compared with the requirement for identification. However, the great deviation in the mass accuracy has been dramatically decreased at the second and third inter-laboratory tests by the accumulating knowledge through the discussion among the WG. Based on the results obtained, a practical guide to analysts for mass scale calibration will be provided in near future.

1. Introduction

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is quite powerful technique for the analysis of practical surfaces. It is spreading widely in both industry and academia for the characterization and understanding of molecular and organic surfaces. Concomitantly, there is a growing realization of the need for a standards base. Thus the ToF-SIMS Working Group (WG) in Surface Analysis Society of Japan (SASJ) was established in June 2007.

At the beginning of our activities the simple survey of the interests in ToF-SIMS among SASJ people was performed at the 30th regular meeting. The questionnaires were as follows:

- Q1. Do you or your colleague use ToF-SIMS?
- Q2. Do you have interests in ToF-SIMS?
- Q3. If you have some interests in ToF-SIMS, which materials are you interested in?
- Q4. If you have some interests in ToF-SIMS, which subjects are you interested in?

To simplify, the answer formula is to mark the number of {1, 2, 3, 4 and 5} according to the degree

of their interests (1 for lowest; 5 for highest). 36 answer sheets were returned from 59 attendants in the meeting. For Q4, they ranked “the identification of surface chemical species” as the top priority, whereas “the standardization” was ranked as the lowest priority. In order to identify the surface species correctly the accurate calibration of the mass scale is essential to assign a reliable chemical composition to a particular mass peak. However, there are a few studies to provide a guide to analysts for mass scale calibration of ToF-SIMS. Some useful inter-laboratory studies have been conducted by National Physical Laboratory (NPL) [1-4].

To evaluate the present errors in the calibration of the mass scale, ToF-SIMS WG conducted the domestic inter-laboratory studies involving 14 instruments in 2007, 2008 and 2009. The participants are tabulated in Table 1 and all of them belong to the Japanese private companies of various industries. Their instrument model type and primary ion species are listed in Table 2 with their identifying alphabet, A ~ N.

Table 1. Participants in the inter-laboratory tests in 2007, 2008 and 2009.

Name	Affiliation
Y. Abe	Mitsubishi Chemical Group Sci&Tech Research Center
R. Ihara	TDK
S. Iida	Ulvac-Phi
H. Inomata	NSG Techno Research
H. Itoh	Konica-Minolta Technology Center
T. Kawashima	Panasonic Corporation
D. Kobayashi	Asahi Glass
T. Kubo	Ricoh
Y. Mori	NGK Insulators
H. Okuhira	Hitachi High-Tech Trading
S. Otomo	Furukawa Electric
M. Samejima	Hitachi Chemical Techno Service
M. Satoh	Teijin
K. Sugai	Teijin
Y. Takeguchi	Hitachi High-Tech Trading
H. Yasufuku	Ricoh

Table 2. The instrument identifying alphabet with the instrument model type and primary ion species.

Instrument alphabet	Instrument Type	Primary ion species
A	ION-TOF V	Bi_3^{++}
B	TRIFT II	In^+
C	TRIFT V	Au^+
D	TRIFT V	$\text{Au}_3^{++}, \text{Bi}_3^{++}$
E	ION-TOF IV	Bi_3^{++}
F	TRIFT III	Ga^+
G	ION-TOF V	$\text{Bi}^+, \text{Bi}_3^+, \text{Bi}_3^{++}$
H	TRIFT IV	Au^+
I	ION-TOF IV	Ga^+
J	TRIFT IV	Au_3^+
K	TRIFT III	Au^+
L	ION-TOF V	Bi_3^{++}
M	TRIFT IV	Au^+
N	TRIFT II	Ga^+

2. Summary of the inter-laboratory test in 2007

The first inter-laboratory test among SASJ people was conducted in 2007. Two practical samples were delivered to the participants listed in

Table 1. One was a popular UV stabilizer named Tinuvin 770 ($\text{C}_{28}\text{H}_{52}\text{N}_2\text{O}_4$, molecular weight (MW) 480.39 u). This granule was dissolved into acetone and cast on the clean Si wafer by each laboratory. Its molecular ion appears in both positive and negative ion mass spectra. We can examine the effect of the secondary ion polarity. The other was a commercially available CD-R, which had two thin films of a dye layer and a reflective layer between an overcoat and a polycarbonate (PC) substrate [overcoat / reflective layer / dye layer / substrate]. MW of the dye was estimated at 483.28 u. The reflective layer mainly consisted of Ag. At just before the ToF-SIMS measurements the overcoat and the reflective layer were removed with an adhesive tape. We could easily peel them off and got the fresh surface of the dye, which had been protected by the reflective layer. The reflective layer was exposed to the surface on another side. The dye was also detectable from the reflective layer as a residue. Thus, we can compare the ToF-SIMS spectra of the dye on the insulating substrate (PC) and that on the conductive layer (Ag).

The detail information on samples was not open to the participants. Ten laboratories (A ~ J in Table 2) returned the results. They acquired the mass spectra and calibrated the mass spectra by their own local procedures. Peak positions and intensities of molecular ions and typical fragment ions were requested to report. In this test, procedures for data acquisition, mass scale calibration and determination of the peak position were not specified by the conductor. The major purpose was to survey the present deviation in the ToF-SIMS mass scale in Japanese industries.

The results are summarized in Table 3 and Fig. 1 [5, 6]. In the case of Tinuvin 770, the averaged relative mass accuracy of the molecular ions (+/-) is 43 ppm. There are no significant differences between positive ions and negative ions. In the case of CD-R, the averaged relative mass accuracy of the molecular ions is 50 - 80 ppm. The conducting side (on Ag) gives the smaller scatter than the insulating side (on PC), which means that the mass scale calibration is affected by the conditions of electron flood gun for charge compensation. In both samples

there was significant scatter over 100 ppm in the relative mass accuracy. Clearly, this is poor compared with the requirement for identification.

3. Summary of the inter-laboratory test in 2008

The second inter-laboratory test was conducted in 2008. Two commercially available samples were delivered to the participants listed in Table 1. One was a polyethyleneterephthalate (PET) bottle with mineral water and the other was cyan ink for the ink jet printer. The former was cut into the small piece by each laboratory. The latter was dissolved into acetone and cast on the clean Si wafer by each laboratory. However, Si wafer sometimes shed the ink and the uniformity of the sample was not good.

The information on samples was open to the participants, but nobody knows the contents in the ink completely. Eight instruments (A ~ F, H and J in Table 2) returned the results, which are summarized in Table 3 and Fig.3 [7]. The averaged relative mass accuracy for PET bottle and cyan ink was below 30 ppm. However procedures for data acquisition, mass scale calibration and determination of the peak position were not specified by the conductor as well as the previous test, the great scatter in the mass accuracy has been dramatically decreased. We believe that this improvement is one of the fruits of our activities. The knowledge concerning with the sample preparation, spectrum acquisition and mass scale calibration has been accumulated through the discussion among ToF-SIMS WG.

4. Summary of the inter-laboratory test in 2009

The third inter-laboratory test was conducted in 2009. The sample was a commercially available capsule including the supplementary health foods of astaxanthin ($C_{40}H_{52}O_4$, MW 596.39 u) and vitamin E ($C_{29}H_{50}O_2$, MW 430.38 u). At just before the measurements, the capsule was cut into halves and its contents were dissolved into acetone and cast on the clean Si wafer by each laboratory. At the planning of this inter-laboratory test, we believed that the capsuled foods or medicines are desirable for inter-laboratory tests because the capsule prevents its contents from oxidation or other degradation under atmosphere.

In this test several operating parameters for data acquisition were specified, if possible. For example, the scanning area was fixed at $200 \mu\text{m} \times 200 \mu\text{m}$ and the acquisition time was fixed at 200 sec. Peaks used for mass scale calibration were also specified by the conductor. Two combinations of the peaks for mass scale calibration were selected as below:

- a) CH_3^+ , C_2H_3^+ , C_3H_5^+
- b) C^+ , CH^+ , CH_2^+ , C_4H_3^+ , C_4H_5^+
- c) CH^- , C_2H^- , C_4H^-
- d) CH^- , CH_2^- , C_3H^- , C_4H^-

The information on samples was not open to the participants. Twelve instruments (A ~ E, G, H, J ~ N in Table 2) returned the results, which are summarized in Table 3 and Fig.1 [8]. The averaged relative mass accuracy maintains the levels below 30 ppm. In spite of the specification of some operating parameters and the calibration peaks, expected improvements in mass accuracy were not observed. The reason is under discussion in the ToF-SIMS WG [9].

5. Plan of the next inter-laboratory test

We are planning to conduct the final inter-laboratory test for evaluation of the improved accuracy of ToF-SIMS mass scale calibration. Based on the results obtained from the past inter-laboratory tests, the requirements for tested samples can be listed below:

- 1) commercially available (not specially prepared)
- 2) easy to preparation
- 3) not volatile
- 4) not hazardous
- 5) stable under atmosphere
- 6) not roughened
- 7) high secondary ion yield of molecular ions
- 8) molecular weight of around 500 amu

Among the tested samples in the past inter-laboratory tests, the typical UV stabilizer named Tinuvin 770 is selected for the next sample considering the above conditions. To cancel the differences in the sample preparation conditions, such as concentration, solvent, substrate, dropping procedures and so on, the next sample will be delivered as a thin film spin-coated on the clean Si

wafer by the conductor. The analyzing size should be fixed, but the acquisition time can be adapted by the each instrument. Users of monatomic ions like Ga^+ or Au^+ can prolong the acquisition time to obtain the enough counts for determination of the peak position. To cancel the differences in determination of the peak position, the conductors will analyze the all spectra data.

Comparing the results of the next inter-laboratory test with those of the past test in 2007, the effect of the accumulating knowledge through the discussion among ToF-SIMS WG will be expected to reveal. It will make the base for providing the guide for mass scale calibration of ToF-SIMS. We believe that the relative mass accuracy of below 20 ppm for 500 amu will be achievable with the modern ToF-SIMS instruments.

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Table 3. Obtained relative mass accuracy for the characteristic ions of tested materials.

	Tested Material	Mass Calibration	Target Ion	Calculated Mass	Observed Relative Mass Accuracy (ppm)		
					max	min	average
2007	Tinuvin 770	Each Local Procedure	[M+H](+)	481.4005	134.75	-58.02	42.85
			[M-H](-)	479.3849	133.96	-22.28	42.55
	Dye on PC Dye on Ag	Each Local Procedure	[M](+)	483.2800	227.36	-129.99	77.45
			[M](+)	483.2800	52.10	-96.47	52.37
2008	PET Bottle	Each Local Procedure	[M-H](-)	191.0344	66.83	11.86	28.19
			[M+H](+)	193.0501	70.53	-42.39	28.53
			[3M+H](+)	577.1346	51.46	-35.00	28.47
	Cyan Ink for IJ Printer	Each Local Procedure	[M+Na](+)	557.3666	-6.19	-68.27	27.77
2009	Vitamin E	Fixed {CH ₃ , C ₂ H ₃ , C ₃ H ₅ }	[M](+)	430.3811	14.68	-82.00	30.90
		Fixed {C, CH, CH ₂ , C ₄ H ₃ , C ₄ H ₅ }	[M](+)	430.3811	85.97	-72.38	34.09
		Fixed {CH, C ₂ H, C ₄ H}	[M-H](-)	429.3733	78.02	-20.96	26.74
		Fixed {CH, CH ₂ , C ₃ H, C ₄ H}	[M-H](-)	429.3733	45.88	-50.54	28.07

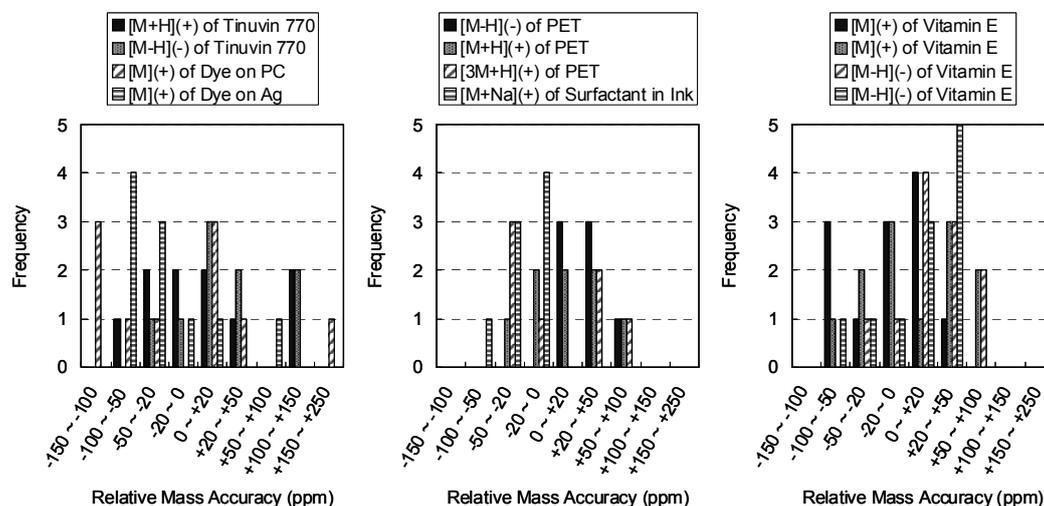


Fig.1. Histograms of the obtained relative mass accuracy.