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Surface chemical analysis — Secondary-ion mass spectrometry — Repeatability and constancy of the relative-intensity scale in static secondary-ion mass spectrometry

Analyse chimique des surfaces — Spectrométrie de masse des ions secondaires — Répétabilité et constance de l'échelle des intensités relatives en spectrométrie statique de masse des ions secondaires

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Contents

Page

Foreword

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ISO 23830 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 6, *Secondary ion mass spectrometry*.

Introduction

Static secondary-ion mass spectrometry (SIMS) is used extensively for the surface analysis of complex materials. Static SIMS is most often used for identification of materials at surfaces and for the quantification of mixtures, for example functionalized-surface polymer blends. Quantification is usually achieved through measuring relative peak intensities and by comparing these with appropriate peaks from reference materials. Repeatability is important for these measurements in order to understand if any variations observed are significant. The constancy of relative intensities is important for relating work historically to databases as well as establishing the instrument behaviour. Many static SIMS measurements are for the purpose of identification of an unknown material through the use of pattern matching with spectral libraries. The extent to which this is meaningful depends on the instrument repeatability and stability. There are two important instrumental contributions to the uncertainty of static SIMS intensity measurements that are addressed in this International Standard: (i) the repeatability of positive-ion relative-intensity measurements and (ii) the drift of the positive-ion relative intensities with time. With negative ions, the control of the surface potential for insulators is not yet sufficiently good for high repeatability. Consequently, negative ions are not included in this International Standard, although it is possible that the concept described will work for negative ions if the surface potential control problem is solved.

Repeatability is important for analysing the trends and differences between samples that are similar. Poor repeatability can erroneously give the conclusion that the samples are significantly different. The instrumental issues that limit the measurement repeatability include the stability of the ion source, charge stabilization, the settings of the detector, the sensitivity of the instrument to the sample placement, the data-acquisition parameters and the data-processing procedure.

This International Standard describes a simple method for confirming the repeatability and constancy of the relative-intensity scale of the instrument so that the instrument behaviour is characterized and that any remedial action, such as improving the operating procedure or resetting of the instrument parameters, may be made. This method should, therefore, be conducted at regular intervals and is most useful if the data include a period in which the instrument has been checked to be working correctly by the manufacturer or other appropriate body. This method uses a sample of poly(tetrafluoroethylene), which is abbreviated to PTFE, and is applicable to static SIMS spectrometers with charge stabilization.

This method does not address all of the possible defects of instruments since the required tests would be very time-consuming and need both specialist knowledge and equipment. This method is, however, designed to address the basic common problem of repeatability and of drift of the relative-intensity scales of static SIMS instruments.

Surface chemical analysis — Secondary-ion mass spectrometry — Repeatability and constancy of the relative-intensity scale in static secondary-ion mass spectrometry

1 Scope

This International Standard specifies a method for confirming the repeatability and constancy of the positive-ion relative-intensity scale of static secondary-ion mass spectrometers, for general analytical purposes. It is only applicable to instruments that incorporate an electron gun for charge neutralization. It is not intended to be a calibration of the intensity/mass response function. That calibration may be made by the instrument manufacturer or another organization. The present method provides data to confirm the constancy of relative intensities with instrument usage. Guidance is given on some of the instrument settings that may affect this constancy.

2 Symbols and abbreviations

A_1	average combined peak area for the C_3F_3 and C_2F_5 peaks
A_2	average combined peak area for the C_7F_{13} and C_8F_{15} peaks
A_3	average combined peak area for the $C_{14}F_{27}$ and $C_{15}F_{29}$ peaks
d	beam diameter (µm)
e	charge on the electron (C)
F	pulse repetition rate or frequency (s^{-1}) (required for time-of-flight systems only)
i	index for the ith of the 13 mass peaks
I_{ij}	matrix of peak intensities for the ith mass peak and jth spectrum
$\bar{I}_i$	average peak intensity over the seven spectra
j	index for the jth of the seven spectra
J	total ion fluence (ions·m^{-2})
n	number of complete raster frames
N_{ij}	matrix of normalized peak intensities for the ith mass peak and jth spectrum
p	number of ion pulses delivered per pixel (required for time-of-flight systems only)
P_{ij}	matrix of relative peak intensities for the ith mass peak and jth spectrum
$\bar{P}_j$	average relative peak intensity over nine mass peaks of the jth spectrum

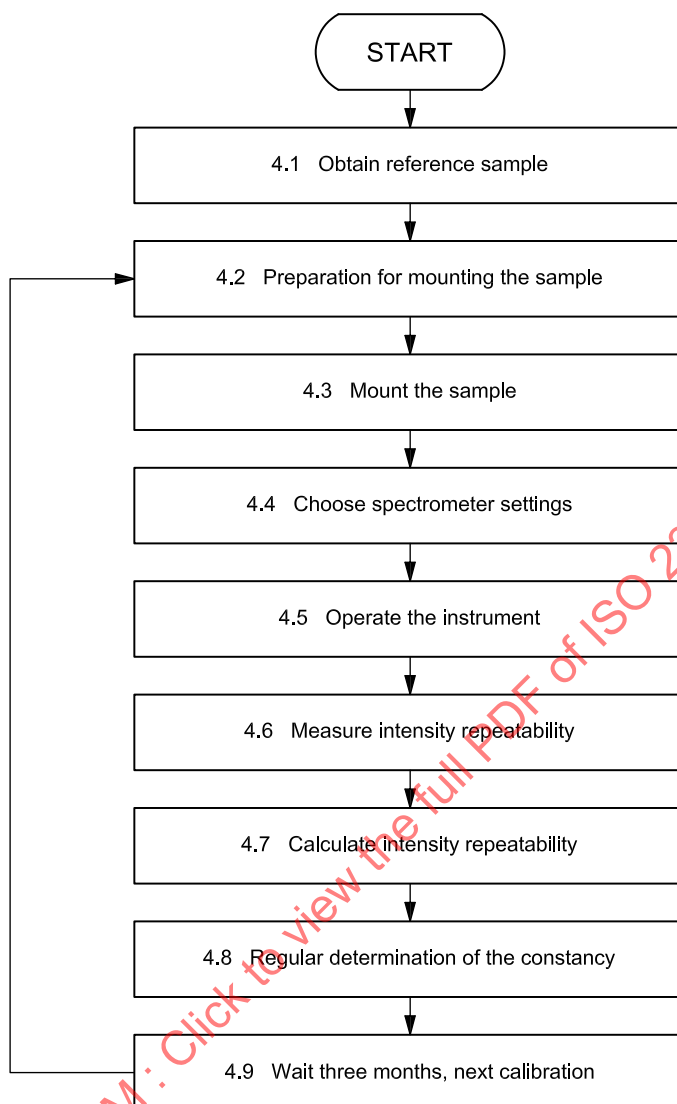| q | time-averaged pulsed ion beam current (A) (required for time-of-flight systems only) |
Q	ion beam current (A) (required for non-pulsed systems and for some time-of-flight systems)
r	relative-intensity repeatability
R	length of side of square raster (μm)
SIMS	secondary-ion mass spectrometry
T	total spectrum acquisition time (s)
ToF	time of flight
u	unified atomic mass unit
$U_{95}(A_1/A_2)$	uncertainty in A_1/A_2
$U_{95}(A_3/A_2)$	uncertainty in A_3/A_2
w	pulse width (s)
X	number of pixels along a line of the raster

3   Outline of method

Here, the method is outlined so that the detailed procedure, given in Clause 4, may be understood in context. To evaluate a static SIMS spectrometer using this procedure, obtain a fresh reel of PTFE tape, of the type used for domestic plumbing, in order to measure the intensities of selected SIMS mass peaks with appropriate instrumental settings. This material is chosen because it is readily available, has low surface contamination and has been well characterized by static SIMS to have the surface uniformity to achieve excellent levels of repeatability. The peaks are chosen to exhibit no mass interference and so the procedure is relevant to instruments with both high and low mass resolution.

The initial steps of procuring the sample and setting up the instrument are described in 4.1 to 4.5 and shown in the flowchart in Figure 1 with the relevant paragraph headings paraphrased.

In 4.6, mass spectra are acquired in a sequence repeated seven times. These data give the repeatability standard deviations of the peak intensities. These repeatabilities have contributions from the stabilities of the ion source, the surface charge on the sample, the spectrometer detector and the electronic supplies, as well as from the sensitivity of the measured peak intensity to the sample position and from the statistical noise in the peak. In the method, conditions are defined to ensure that the statistical noise of the measured intensities is relatively small. The value of the repeatability standard deviation may depend on the sample-positioning procedure. In 4.6.1, the use of a consistent sample-positioning procedure is required and the final calibration is only valid for samples positioned using this positioning procedure.

Generally, for static SIMS, the relative peak intensities, rather than the absolute intensities, are most important for material identification. In this method, therefore, the scope is limited to determining the constancy of the relative intensities. These determinations are made in 4.7 and their calculation defined in 4.8, as shown in the flowchart in Figure 1.

In practice, the intensity/mass response function of spectrometers may change significantly with instrument use and especially between different operators of the same instrument. It may therefore be useful for each analyst to conduct this procedure. The interval between repeat assessments is given in 4.9. It is imperative that the instrument be operated using a documented procedure to help minimize variations in spectral response.

START

4.1   Obtain reference sample

4.2   Preparation for mounting the sample

4.3   Mount the sample

4.4   Choose spectrometer settings

4.5   Operate the instrument

4.6   Measure intensity repeatability

4.7   Calculate intensity repeatability

4.8   Regular determination of the constancy

4.9   Wait three months, next calibration

Figure 1 — Flowchart of the sequence of operations of the method
(Subclause numbers are given with items for cross-referencing with the body of the text.)

4   Method for confirming the repeatability and constancy of the intensity scale

4.1   Obtaining the reference sample

For the calibration of static SIMS spectrometers, obtain a new reel of PTFE tape of the type used for domestic plumbing. Label this reel and keep it with your reference samples for later checks in 4.9.

NOTE   The PTFE is usually in the form of a reel of tape of length 12 m and width 12 mm and approximately 0,075 mm thick.

4.2   Preparation for mounting the sample

Samples shall only be handled with clean metal tweezers held using powderless polyethylene gloves. Vinyl gloves, often used in clean rooms, are coated with a release agent from the moulding process and shall not be used. The release agent is very mobile and quickly contaminates the samples. This leads to poor measurement repeatability and poor-quality data.

4.3   Mounting the sample

Remove and discard the first 20 cm of material from the reel obtained in 4.1 and then cut appropriately sized samples from the subsequent material with clean scissors. As the reel is unwound, a fresh surface of PTFE is exposed and it is this surface that is analysed. Do not clean the sample. Mount samples on the sample holder to produce a flat, even surface using a mechanical clamping or fixing method. Do not use adhesive tape. Ensure that the reverse side of the sample is against a conducting surface, electrically connected to the sample holder. The PTFE shall not be placed over a hole.

NOTE   The presence of a hole under the sample leads to poor mass resolution and repeatability in systems that use high extraction fields, such as time-of-flight and magnetic-sector systems.

Repeat measurements are required later in 4.9 at intervals of no longer than three months. For this, a fresh sample is required and, for consistency, the sample should be from the same reel.

4.4   Choosing the spectrometer settings for which intensity stability is to be determined

Choose the spectrometer operating settings for the positive secondary ions for which the intensity stability is to be determined. The method from 4.5 to 4.9 shall be repeated for each ion source for which confirmation is required.

NOTE   The repeatability of the relative intensities varies with the combination of settings used. In general, the repeatability will be best when using an energy acceptance of the mass analyser of 50 eV or more.

4.5   Operating the instrument

4.5.1   Operate the instrument in accordance with the manufacturer's or local documented instructions. The instrument shall have fully cooled following any bakeout. Ensure that the operation is within the manufacturer's recommended ranges for ion beam current, counting rates, spectrometer scan rate and any other parameter specified by the manufacturer. Check that the detector multiplier settings are correctly adjusted.

4.5.2   Centre the ion beam in the acceptance area of the mass spectrometer. Ensure that the ion beam focus diameter, d, is sufficiently defocused such that

$$d > \frac{2R}{X} \tag{1}$$

for a square raster with side of length R and where X is the number of pixels along a line of the raster. If it is found that the maximum achievable beam diameter in the instrument is too small to satisfy Equation (1), the number of pixels will need to be increased or the raster size reduced.

4.5.3   Select values of the time-averaged pulsed ion beam current, q, the total acquisition time, T, and the raster size, R, to give an ion fluence, J, of $< 1 \times 10^{16}$ ions·m^{-2}. J is given by

$$J = \frac{qT}{eR^2} \tag{2}$$

For non-pulsed instruments, such as magnetic-sector and quadrupole-based systems, use Equation (2) but with the pulsed current, q, substituted by the non-pulsed current, Q.

For some ToF instruments, q is not known and the non-pulsed current, Q, is recorded instead, in which case

$$J = \frac{FQwT}{eR^2} \tag{3}$$

where

   F is the frequency of the ion pulses;

   w is the ion beam pulse width (without pulse beam bunching).

EXAMPLE   A 0,5 pA beam (either ToF instrument pulsed beam current or the non-pulsed beam current for a quadrupole or magnetic-sector instrument) with a 200 µm square raster and 128 s acquisition time would need to be defocused to a diameter greater than 3,1 µm for a 128 × 128 pixel display. If it can only be defocused to 1 µm, a 256 × 256 pixel display needs to be used or the local fluence on a pixel, given by the 1×10^{16} ions·m^{-2} limit, will be exceeded by a factor of more than 2.

The total acquisition time, T, is the total time that the ion beam impacts the sample surface. For pulsed systems, this includes the full cycle time, not just the time width of the ion pulse at the surface. Some instrument computers, especially for ToF instruments, report a "total time" which includes computer-processing time when the ion beam is blanked and an "acquisition time" which does not include the additional computer-processing time. In this case, use the "acquisition time" value. Terms used in commercial instruments may not be consistent with the terms used here.

4.5.4   For magnetic-sector and quadrupole instruments, operate in a spectroscopy mode using a high-speed scan rate (typically at television rates) rather than the digital raster used for imaging purposes. If you need to use the digital raster, use an acquisition time to acquire an integer number of frames, n, above 20, if possible.

For ToF systems, acquire an integer number of frames, n, above 20, if possible. If you cannot acquire an integer number of frames, n, then, to ensure homogeneous sampling over the raster area, n should be kept above 20 provided the analysis is across a uniform area of spectrometer transmittance. If this is uncertain, use 100 frames. This ensures that the final frame, which most likely will not be a full frame, represents only a small fraction of the data. The number of frames, n, with p ion pulses per pixel is given by

$$n = \frac{TF}{X^2 p} \qquad (4)$$

NOTE   For ToF instruments, typically, $p = 1$ for spectroscopy.

4.5.5   Measure the ion beam current density, J, with the raster operational and using, if available, a suitable Faraday cup. If your system does not have a Faraday cup, a simple but accurate device may be made by drilling a small hole in a sample holder, aligned to the ion beam axis and with a depth greater than five times the diameter. The diameter shall be in the range 0,1 mm to 1 mm.

NOTE   Details of Faraday cup behaviour may be found in Reference [1].

4.5.6   At high primary-ion beam currents, a significant fraction of counts are lost through detector saturation. Ensure that the primary-ion beam current is below a level at which < 2 % of counts are lost through detector saturation.

Primary ions of mass > 70 u or primary ions composed of clusters may cause peak saturation even at low primary-ion currents. This is usually manifested by reduced or complete loss of intensities in the mass range following the saturated peak. For Bi$^+$, a pulsed ion beam current of no more than 0,1 pA is recommended.

4.5.7   For maximum efficiency of ion detection, set the impact energy of the detected ions at the detector surface to the maximum stable value that does not contribute significantly to the background noise.

NOTE   High counting rates[2] or incorrect detector voltages[3] can cause peak distortions that lead to erroneous peak intensity measurements.

4.5.8   A proper charge stabilization procedure is essential for obtaining good measurements. Use the manufacturer's procedure or a local documented procedure. Ensure that your procedure is clear and complete.

NOTE   Guidance for charge stabilization is provided in References [4] and [5].

4.6 Measurements of the intensity and its repeatability

4.6.1 Set the PTFE sample mounted in 4.3 at the same analytical position as is normally used. The sample-positioning procedure shall follow a documented protocol that takes account of the manufacturer's recommendations.

4.6.2 Select the settings chosen in 4.5 and an acquisition time defined by Equation (2) or Equation (3). For ToF instruments, select a repetition rate that gives a maximum mass of at least 800 u. For scanning mass spectrometers, such as quadrupole and magnetic-sector mass spectrometers, record only the mass peaks selected in Table 1, in descending order of mass. If the total counts in the $C_{14}F_{27}$ and $C_{15}F_{29}$ peaks are less than 100 counts, increase the acquisition time to ensure that these peaks contain more than 100 counts, unless the signal is very weak. To ensure that the maximum ion fluence is not exceeded, an enlarged raster area may be required. The acquisition time finally chosen will be a compromise between the data quality and the duration of the work. Record the parameters you set.

NOTE   The weakest peaks are likely to be $C_{14}F_{27}$ and $C_{15}F_{29}$.

For weak spectra, the repeatability will be poor. Use a spectrum acquisition time of 10 min. If the two weakest peaks have 100 counts each, the repeatability for these peaks, for a confidence level of 95 %, is 20 % each.

Table 1 — Values of the mass of each fragment to be recorded in various situations

Index, i	Fragment	Use (see key)	Mass u
1	CF_2	b	49,996 8
2	CF_3	a	68,995 2
3	C_3F_3	b	92,995 2
4	C_2F_5	b	118,992 0
5	C_3F_5	a	130,992 0
6	C_4F_6	b	161,990 4
7	C_4F_7	a	180,988 8
8	C_5F_7	a	192,988 8
9	C_5F_9	a	230,985 6
10	C_7F_{13}	c	330,979 2
11	C_8F_{15}	c	380,976 0
12	$C_{14}F_{27}$	c	680,956 9
13	$C_{15}F_{29}$	c	730,953 7

Key

a   for intensity repeatability

b   as "a" and also used for mass calibration

c   used only for constancy of the relative-intensity scale

4.6.3 Acquire seven positive-ion spectra. A fresh area of material shall be analysed with a total fluence of less than 1×10^{16} ions·m^{-2} (1×10^{12} ions·cm^{-2}) each time. All analysis areas shall be at distances greater than 1,5 mm from the edge of the sample holder. For a square raster of side R, the recommended minimum repeat distance (centre to centre) between rasters is 2,5R.

NOTE   With a raster area of $R = 200$ µm, the minimum repeat distance between each raster is 500 µm with a minimum gap between each raster area of 300 µm.

4.7 Calculating the intensity repeatability

4.7.1 For ToF spectrometers, calibrate the mass scale for each spectrum using the exact masses of the peaks labelled "b" in Table 1. To assist in identifying them, these calibration peaks are denoted by an arrow in Figure 2. For other spectrometers, confirm that the mass of the maximum intensity for each peak is within $\pm 0{,}1$ u of the exact mass. If the mass peaks are outside this range, recalibrate the instrument using a documented procedure.

4.7.2 To ensure maximum linearity of the intensity scale, use the dead-time-correction procedure provided by the instrument manufacturer or other locally documented procedures.

4.7.3 For each of the seven measurements of each mass peak, sum the dead-time-corrected intensities within the mass limits $\pm 0{,}5$ u of the mass position defined in Table 1. For high mass resolution instruments, the mass interval between the limits may be reduced. Keep a record of these limits and use them for all subsequent measurements in this International Standard. Record the peak areas, I_{ij}, for the 13 mass peaks, i, and the seven spectra, j.

For high mass resolution instruments using gallium primary ions, avoid including Ga^+ (68,925 6 u) in the CF_3^+ peak.

Key

X   mass (u)

Y   number of counts
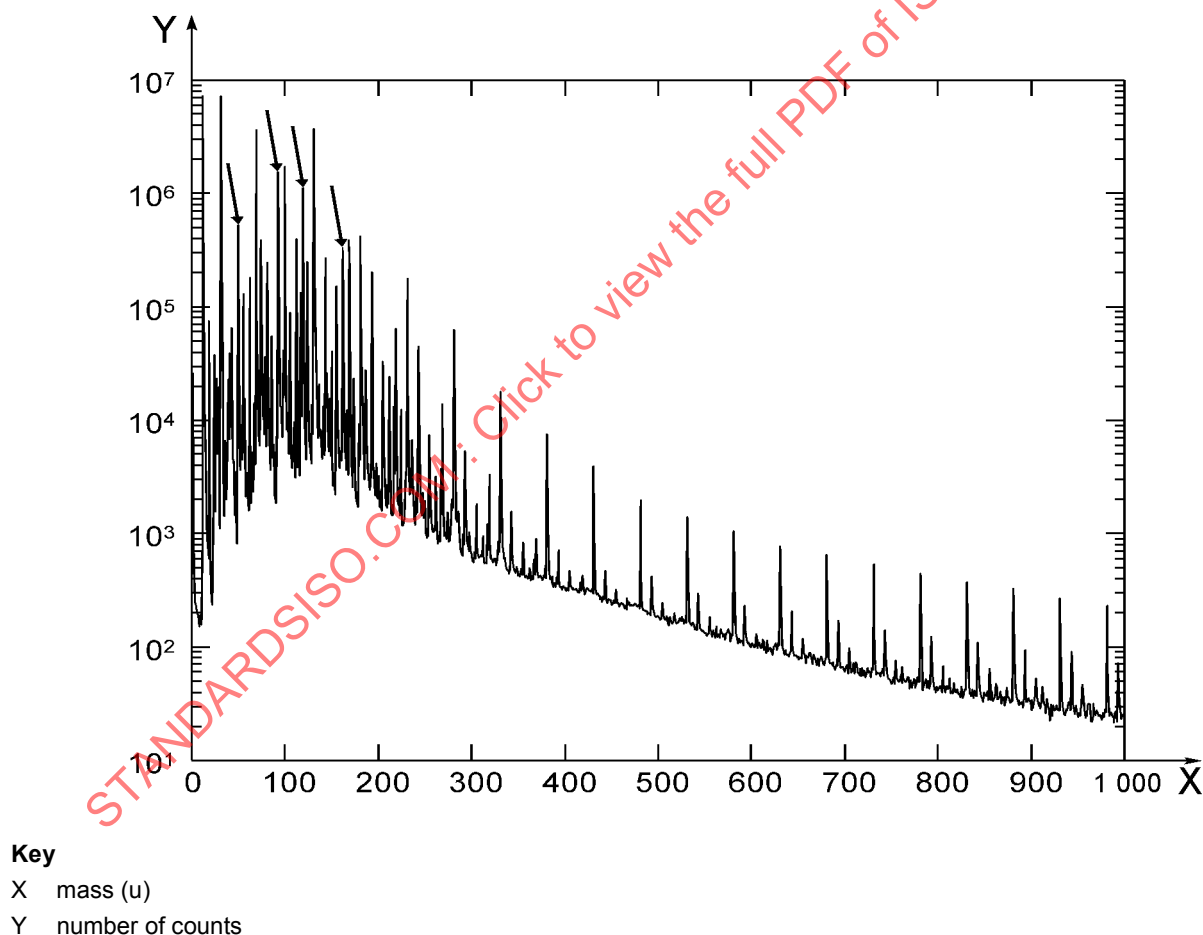
Figure 2 — Example of a positive-ion static SIMS spectrum of PTFE, produced using 15 keV gallium primary ions and a ToF mass spectrometer operated under the conditions given in Annex A
(The arrows indicate the positions of the peaks used in calibration of the mass scale.)

4.7.4   Review the seven values of each of the peak area intensities for the 13 mass peaks for any systematic changes with time through their order of acquisition. Such systematics may indicate an inadequate warm-up period, a change in the laboratory temperature, an inadequate detector voltage or another source of drift. If this appears to be the case, take appropriate action (for example, increase the warm-up period) and repeat 4.6.

4.7.5   Calculate the average intensity, $\bar{I}_i$, for each mass from the seven spectra using the following equation:

$$\bar{I}_i = \frac{1}{7}\sum_{j=1}^{7} I_{ij} \tag{5}$$

Then divide each intensity, I_{ij}, by the relevant average, $\bar{I}_i$, to determine the relative strength, P_{ij}, in each peak:

$$P_{ij} = \frac{I_{ij}}{\bar{I}_i} \tag{6}$$

NOTE   The values of P_{ij} are all approximately unity.

4.7.6   For the nine peaks labelled "a" and "b" in Table 1, calculate the average strength, $\bar{P}_j$, in the spectrum, j, which depends on the beam current, etc., using the following equation:

$$\bar{P}_j = \frac{1}{9}\sum_{i=1}^{9} P_{ij} \tag{7}$$

NOTE   Only the first nine peaks are used to calculate repeatability. The four additional peaks calculated for $\bar{I}_i$ are used later in 4.8 to measure the constancy of the relative-intensity scale.

The average strength, $\bar{P}_j$, is now removed from each spectrum intensity by forming the normalized intensities, N_{ij}, for the peaks $i = 1$ to $i = 9$ only.

$$N_{ij} = \frac{P_{ij}}{\bar{P}_j} \tag{8}$$

4.7.7   Calculate the spectral relative-intensity repeatability as follows. The scatter in the relative intensities of each peak is now given by the standard deviation of the N_{ij} for each given mass, i, in the set of spectra, j.

$$\left[\sigma(N_i)\right]^2 = \sum_{j=1}^{7} \frac{(N_{ij}-1)^2}{6} \tag{9}$$

The SIMS relative-intensity repeatability, r, is defined as the average of these standard deviations over the first nine mass peaks:

$$r = \frac{1}{9}\sum_{i=1}^{9} \sigma(N_i) \tag{10}$$

NOTE 1   The values of N_{ij} will all be approximately unity.

NOTE 2   Examples of analyses using this method can be found in References [5], [6] and [7].

4.7.8   Record the value of the repeatability, r, the instrument operating conditions and the date in the instrument log.

4.8 Procedure for the regular determination of the constancy of the relative-intensity scale

4.8.1 For the regular determination of the constancy of the relative-intensity scale, a simple procedure is used for spectrometers operating up to 800 u involving only six of the 13 peaks.

4.8.2 For the regular assessment of the constancy of the spectrometer intensity scale, determine the average values A_1, A_2 and A_3 from the average intensities, $\bar{I}_i$, determined in 4.7.5, as follows:

$$A_1 = \frac{1}{2}\left(\bar{I}_3 + \bar{I}_4\right) \tag{11}$$

$$A_2 = \frac{1}{2}\left(\bar{I}_{10} + \bar{I}_{11}\right) \tag{12}$$

$$A_3 = \frac{1}{2}\left(\bar{I}_{12} + \bar{I}_{13}\right) \tag{13}$$

NOTE   The peaks relating to these intensities are listed in Table 1 and the intensities with indices 3, 4, 10, 11, 12 and 13 are for the C_3F_3, C_2F_5, C_7F_{13}, C_8F_{15}, $C_{14}F_{27}$ and $C_{15}F_{29}$ peaks, respectively.

4.8.3 Plot a control chart for the ratio A_3/A_2 and the ratio A_1/A_2, as illustrated in Figure 3. Define a percentage limit, $\pm \delta$, for the relative-intensity constancy with which you wish to operate the instrument. Plot these control limits for your chosen percentage change in A_3/A_2 and A_1/A_2 on the relevant control chart, as shown in Figure 3. Add warning limits at $\pm 0,7\delta$.

NOTE   Typical values of A_1/A_2 and A_3/A_2 are 105 and 0,045, respectively [7].

4.8.4 Calculate the uncertainty $U_{95}(A_1/A_2)$ in A_1/A_2 from

$$U_{95}(A_1/A_2) = k\frac{A_1}{A_2}\left\{\left[\frac{1}{7\left(\bar{I}_3 + \bar{I}_4\right)}\right] + \left[\frac{1}{7\left(\bar{I}_{10} + \bar{I}_{11}\right)}\right]\right\}^{0,5} \tag{14}$$

and $U_{95}(A_3/A_2)$ in A_3/A_2 from

$$U_{95}(A_3/A_2) = k\frac{A_3}{A_2}\left\{\left[\frac{1}{7\left(\bar{I}_{12} + \bar{I}_{13}\right)}\right] + \left[\frac{1}{7\left(\bar{I}_{10} + \bar{I}_{11}\right)}\right]\right\}^{0,5} \tag{15}$$

In Equations (14) and (15), k is taken as 2 for a confidence level of 95 %. Plot $U_{95}(A_1/A_2)$ and $U_{95}(A_3/A_2)$ as error bars for A_1/A_2 and A_3/A_2, respectively, in a plot as shown in Figure 3.

NOTE 1   The relative standard deviation of the absolute values of $\bar{I}_i$ may be significantly higher than the relative standard deviation of the ratios. This arises from systematic effects from one spectrum to another that have a common influence on all peaks within a spectrum and therefore do not affect the relative uncertainties calculated in Equations (14) and (15).

NOTE 2   Equations (14) and (15) assume that the only source of uncertainty in the peak ratios is the ion-counting fluctuations that obey Poisson statistics, and that the values of $\bar{I}_i$ are measured as ion counts.
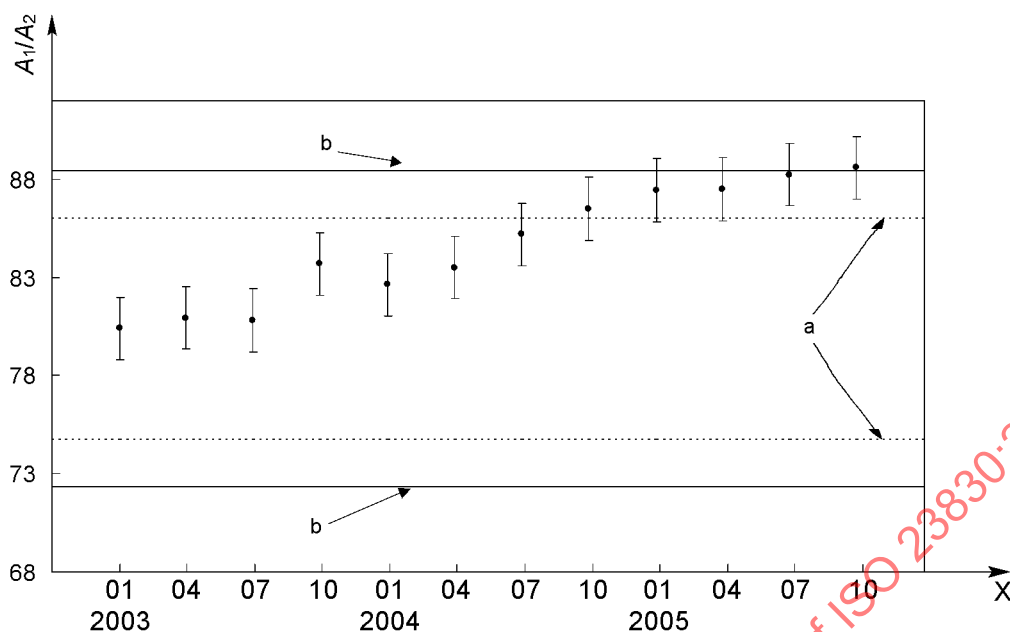
Key

X   measurement date (month)

01   January

04   April

07   July

10   October

a   Warning limits.

b   95 % tolerance limit.

Figure 3 — Schematic control chart [8], [9], of the same kind as that in Reference [10], with tolerance limits set for 10 % drift, to monitor the relative-intensity constancy of an instrument
(The plotted points represent the values for A_1/A_2 which, here, are shown to illustrate an instrument that has not been adjusted since the start in January 2003. It is first out of adjustment in January 2005 and should, since it passed the warning limit, have been readjusted in July 2004. A similar control chart is constructed for A_3/A_2.)

4.9 Next calibration

Following any significant modification or adjustment to the instrument, or once every three months that the instrument is in use, repeat 4.2 to 4.8, using the same conditions as defined in 4.5 and 4.6, to analyse a fresh sample and add the data to the control chart. If the sum of, or difference in, the value of A_1/A_2 and $U_{95}(A_1/A_2)$, and similarly for A_3/A_2, reaches the warning limit, the instrument shall be checked and adjusted or the alignment procedure revised so that new measurements of A_1/A_2 and A_3/A_2 with the associated U_{95} are obtained fully within the acceptance zone.