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Surface chemical analysis — Secondary ion mass spectrometry — Method for the measurement of mass resolution in SIMS

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Foreword

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

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Mass resolution is one of the most important instrumental parameters in mass spectrometry (MS). For any MS experiments, an unambiguous result can only be acquired if sufficient mass resolution is reached to separate the target analytes from any possible interference. If the mass resolution of the instrument is insufficient, it can result in a false positive or negative signal. Therefore, the mass resolution is the primary consideration for determining whether an instrument is adequate for the intended purpose. For routine applications, the mass resolution should be adjusted based on the analytical requirements of the sample. Mass resolution is important not only for the instrument acceptance tests and fundamental studies, but also for almost all routine applications.

This document gives guidance for the measurement of mass resolution in SIMS. Various definitions of mass resolution have been summarized and common problems with popular definitions have been discussed elsewhere[18]. To compare mass resolution between different instrument or/and different types of instruments (e.g. TOF-SIMS, Magnetic SIMS, Quadrupole SIMS, Fourier Transform SIMS and Orbitrap-SIMS, etc.), it is necessary to show the measured peak shape and define mass resolution correctly.

After introducing a reasonable new definition for mass resolution and a method considering the peak shape to compare the mass resolution between TOF-SIMS, Magnetic SIMS, Quadrupole SIMS and Fourier Transform SIMS, this document specifies a method to measure the mass resolution in SIMS.

Surface chemical analysis — Secondary ion mass spectrometry — Method for the measurement of mass resolution in SIMS

1 Scope

This document specifies a method for measuring the mass resolution in SIMS, and how to compare the mass resolution between different instruments (e.g. TOF-SIMS, Magnetic SIMS, Quadrupole SIMS, Fourier Transform SIMS, etc.) by considering the peak shapes.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 18115-1, *Surface chemical analysis — Vocabulary — Part 1: General terms and terms used in spectroscopy*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18115 and the following apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
mass resolution
measurement of the ability of a mass spectrometer to separate mass peaks in a mass spectrum

Note 1 to entry: For a mass peak at position M and a mass peak at position $M+\Delta M$ which can be separated in a mass spectrum then ΔM is the mass resolution of the mass spectrometer at M under these conditions. The peak shape as well as the method of measurement of ΔM should be reported.

Note 2 to entry: If M and $M+\Delta M$ can be separated, ΔM, $M/\Delta M$ or $\Delta M/M$ are defined as mass resolution, mass resolving power or relative mass resolution respectively. Designs of mass spectrometer generally maintain the resolution either to be constant throughout the mass spectrum or to be proportional to mass being scanned. For the former, the mass resolution is a useful term whereas, for the latter, the relative mass resolution and resolving power are more useful.

Note 3 to entry: The sensitivity required to detect the presence of a peak at a position $M+\Delta M$ depends upon the shape of the peak at M and the degree to which peak tails place limits on the magnitude of a peak at $M+\Delta M$ which can be detected. Simple measures of resolution may not represent the actual or practical resolution needed for particular applications.

Note 4 to entry: Usually, normalized output signal distribution from an instrument is a function of variable input measurand values which arises from a feature with a single measurand value. However, in mass spectrometry community, because “mass” is a single measurand value, the peak shape is normally used for the resolution function.

4 Symbols and abbreviated terms

I_M	Measured intensity at mass peak (cts or cts·s^{-1} or arbitrary unit)
I_p	Current of primary ion beam (nA)
I_g	Current of electron beam for charge compensation (μA)
E_p	Energy of primary ion beam (keV)
ΔM	Mass resolution (m/z)
$\Delta M/M$	Relative mass resolution
$M/\Delta M$	Mass resolving power
TOF-SIMS	Time-of-flight secondary ion mass spectrometer
M-SIMS	Magnetic-sector secondary ion mass spectrometer
Q-SIMS	Quadrupole secondary ion mass spectrometer
Orbitrap-SIMS	Orbitrap secondary ion mass spectrometer
FT-SIMS	Fourier transform secondary ion mass spectrometer
FTICR-SIMS	Fourier transform ion cyclotron resonance secondary ion mass spectrometer
SHRIMP	Sensitive high-resolution ion microprobe
X% valley	Valley between the two adjacent and equal peaks is X% of the peak height
X% peak width	Peak width ΔM shall be measured at X% of the peak height (m/z)
X% peak tail interference	Contribution of the M peak tail to its ΔM adjacent peak is X%
R	Mass resolving power ($M/\Delta M$)

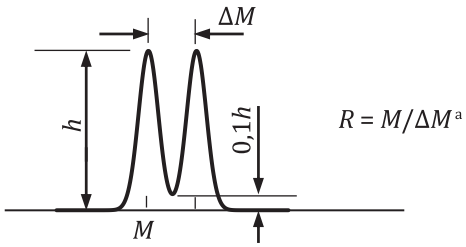
5 Definitions of mass resolution based on peak separations of two mass peaks

5.1 General

There are three different kinds of mass peak separations commonly used for definition of mass resolution, which are summarized as follows.

5.2 X% valley

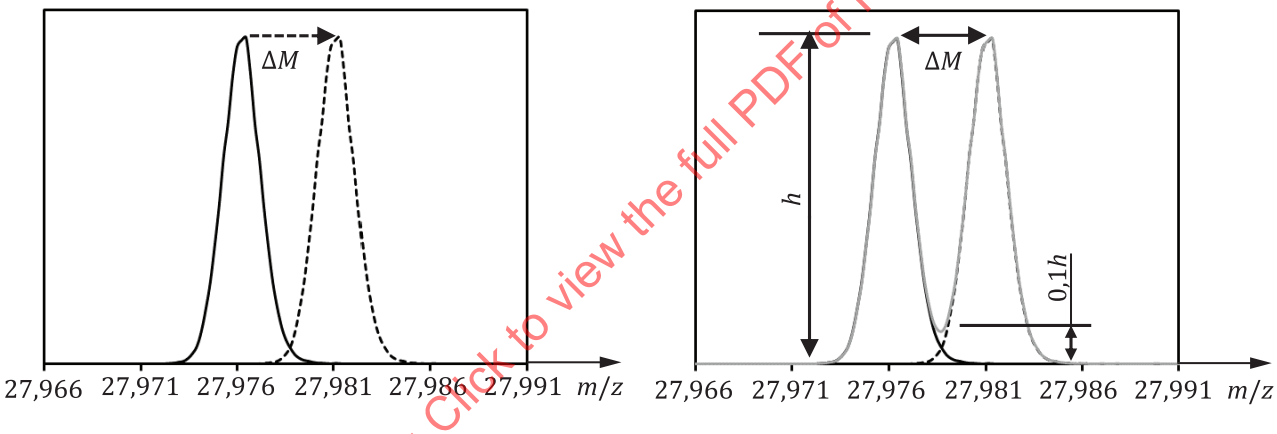
When the valley between two adjacent and equal peaks is X% h, the peak separations of the two mass peaks is ΔM.



[a] Valley ≤ 0,1 h for two adjacent, equal peaks.

Figure 1 — 0,1 h valley between two adjacent and equal peaks

There are rarely standard samples that satisfies the X% valley definition. The following describes how to obtain X% valley for usual standard samples which have only one mass peak. First, select a peak shape without any interference or clean the surface of standard sample to remove any interference of other peaks, then make a second mass peak by copying first peak and compose the two peaks. From the composed peak shape, obtain X% valley. Figure 2 shows how to compose two peaks to obtain X% valley.



Key

——— measured peak

- - - - - - - measured peak after shift Δ*M*

——— sum of the two peaks

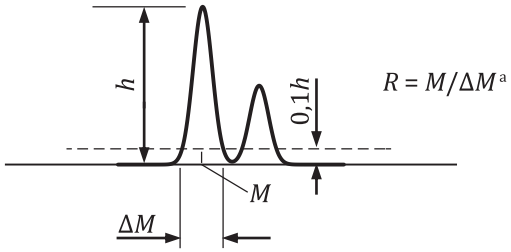
NOTE Here, x=10, 10 % valley, the measured peak is measured by TOF-SIMS on Si wafer

Figure 2 — Two peaks composed from one peak shape to obtain x % valley (x=10, 10 % valley)

As shown in Figure 2 a) another peak is obtained by copying the measured peak with shift ΔM. The two peaks add up so that the intensity of the valley between them is x%h, namely x% valley (here, x=10, 10 % valley) as shown in Figure 2 b).

5.3 X% peak width Δ*M* (X%) or R (X%)=*M*/Δ*M* (X%)

When the peak width measured at X% of the peak height is Δ*M*, the peak separations for two mass peaks is Δ*M*.

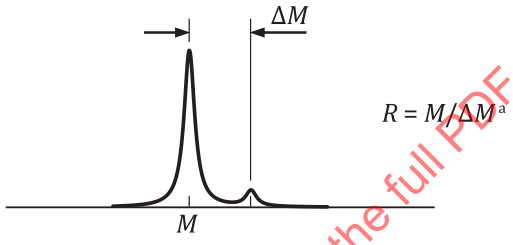


a AT 0,1 h.

Figure 3 — Peak width Δ*M* measured at a point equal to 10 % of the peak height

5.4 X% peak tail interference

When the contribution of the *M* peak tail to its Δ*M* adjacent peak is X%, the peak separations for two mass peaks is Δ*M*.



a 1 % contribution adjacent peaks.

Figure 4 — 1 % contribution of the *M* peak tail to its Δ*M* adjacent peak

NOTE For M-SIMS, abundance sensitivity has been used to describe the peak tail interference. For example, the ratio of the signal intensity can be examined at ^{27}Al ± 27/250 *m/z* [27,089 6 or 26,873 6 *m/z*, next to the mass peak of ^{27}Al (26,981 6 *m/z*)] to the signal intensity of ^{27}Al. The smaller the ratio, the better, generally 0,1 ppm is required for analysing the isotope ratio in geological samples.

5.5 Summary

The physical concept of the valley definition for peak separation is quite clear but it is often difficult to find two adjacent and equal peaks. Therefore, peak fitting or peak composing should normally be used, making the whole process inconvenient.

The peak width is the most popular definition to be used in the field of mass spectrometry. However, there are different X values used in 5.2 to 5.4, which can be selected as 50 %, 20 %, 10 %, 5 %, 1 %, or near 0 %, etc. The 50 % peak width definition is often simplified as full width at half maximum (FWHM) definition. In SIMS analysis, the *R=M/ΔM* (10 %, 1 % or even 0 %) definitions are used for high performance magnetic sector SIMS, and Δ*M* (10 %, 5 %) definitions are used for quadrupole SIMS, but only *R=M/ΔM* (50 %) definition is normally used for TOF-SIMS and FT-SIMS.

In order to perform quantitative analysis, it is necessary to avoid the interference due to contribution of the adjacent peak tail. For example, to analyse the trace ^{27}Al at ^{28}Si wafer by SIMS, it is necessary to avoid the possible interference from the strong ^{28}Si peak tail. In this case, X% peak tail interference definition is commonly used for quantitative analysis.

6 Procedure to determine the mass resolution

6.1 General

For adjusting and optimizing the setting of a SIMS spectrometer, the parameters of analysis (e.g. energy of primary ion, ion species, polarity of secondary ion, scan area of primary ion beam, analysis area, stability of primary ion current, species of secondary ion, etc.) should be set following the procedure given by the maker or industry standard or national standard or international standard.

6.2 Removing contamination on sample surface

The contamination on sample surface should be removed by sputtering or other ways. The contamination layer usually is about 1 nm to 3 nm.

6.3 Obtaining spectrum peak

1) The measured location should be in the area with no or less contamination in the centre of the sample, and at least 0,2 mm away from the edge of the sample.

2) Adjust the current I_p of a beam current and making the maximum of mass spectrum peak within the linear range of detector.

3) Optimize the parameters of primary ion beam and the detection system of secondary ion etc., let the shape of mass peak in mass spectrum as good as possible. The maximum of mass peak is not less than 10^3 counts or the SNR (Signal to Noise Ratio) at mass peak is not less than 10^3.

4) Obtain mass shape by analysing mass spectrum containing interest mass.

6.4 Determination of mass resolution

Mass resolution is determined according to the Clause 5. It is closely related to the peak shape at M and $M+\Delta M$, and how to define peak separation. Therefore, the peak shape as well as the method of measurement of ΔM should be reported in the mass resolution of SIMS.

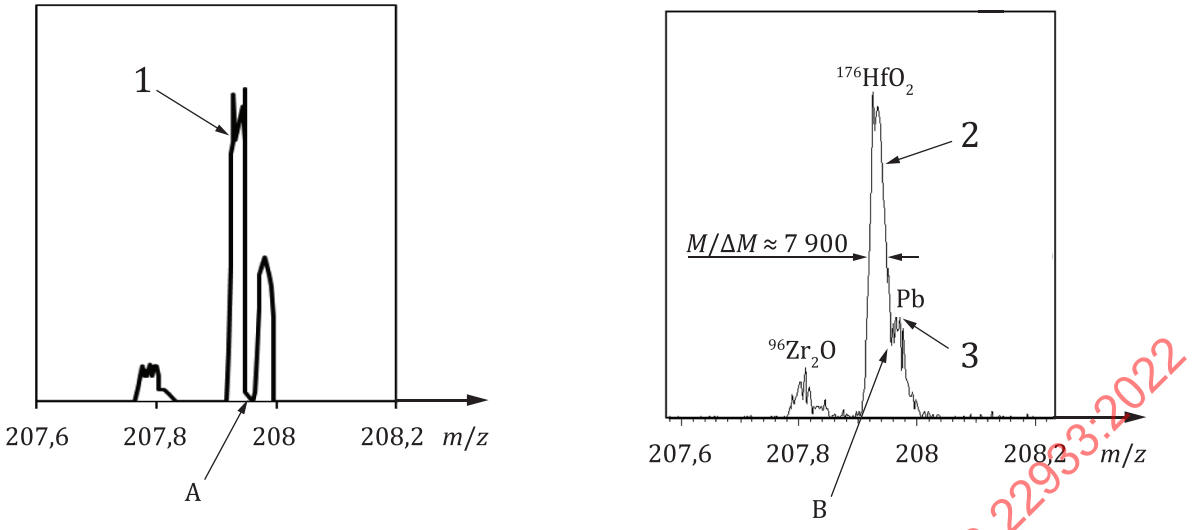
7 Mass resolution comparison between different type of SIMS

7.1 Mass resolution comparison between M-SIMS and TOF-SIMS

TOF.SIMS 5 (TOF-SIMS) from Germany is used to analyse the geological sample to evaluate their mass resolution and make comparison with that of SHRIMP II(M-SIMS). The geological sample used is TEMORA zircon standard sample (also referred to as "TEM"). Several grains of TEM were arranged in the sample holder for U-Th-Pb isotopic measurements and dating. Natural zircon crystals were separated from the rocks at the township TEMORA in Australia.

The analysis parameters used by TOF.SIMS 5 are: Primary Ion: Bi_3^+, Energy: 30 keV, Current: 0,6 pA, Raster: 50 µm×50 µm, Acquiring time: 30 min, Secondary ion: positive ion, Mass range: 0 m/z to 3 000 m/z (Cycle time=200 µs), Flood gun: Ep=20 eV, Ie >10 µA.

Experimental results of ^{208}Pb from TEMORA analysed by TOF.SIMS 5 under with the analysis parameters described in the previous paragraph and compared with Shrimp II are shown in Figure 5. If the definition of mass resolution is based on the peak separation of X% peak width ΔM (X%) or R (X%)=$M/\Delta M$ (X%) for X%=50 %. $M/\Delta M$=7 900 for TOF-SIMS, 7 000 for Shrimp II. From the SHRIMP result, it is clear that the mass peak of ^{208}Pb is separated from $^{176}HfO_2$ completely. However, for the TOF-SIMS result, the mass peak of ^{208}Pb is just starting to separate from $^{176}HfO_2$ after several rounds of careful adjustments. The real mass separation performance between the two different types of instruments has been compared clearly. The relevant details are described in Annex A.



Key

1 measured by SHRIMP II

2 measured by TOF.SIMS 5

3 ^{208}Pb peak

A Completely separated peak of ^{208} Pb from ^{176} HfO_2.

B Peak of ^{208} Pb starting to separate from the ^{176} HfO_2 peak.

Figure 5 — Experimental results of ^{208}Pb from TEMORA by TOF.SIMS 5 and compared with SHRIMP II

It is necessary to mention that the above experimental study is preliminary and can be improved. However, it is confirmed that comparison of the mass resolution between TOF and magnetic SIMS has been realized by considering the measured peak shapes. Table 1 and Table 2 shows mass resolution(ΔM) and mass resolving power($M/\Delta M$) for different definition in M-SIMS and TOF-SIMS, respectively.

Table 1 — Mass resolution(ΔM) of different definition for M-SIMS and TOF-SIMS

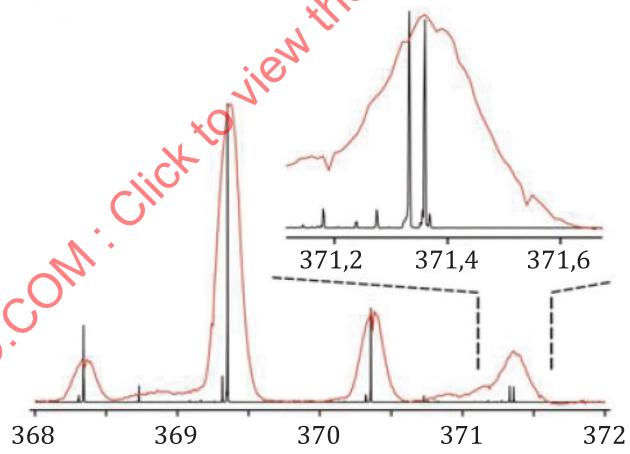
Instrument	Sample	*m/z*	Mass resolution (ΔM)						
			X % valley		X % peak width			X % peak tail interference	
			10 %	1 %	50 %	10 %	1 %	10 %	1 %
TOF	TEMORA Zircon Standard	207,931	0,068 0	0,091 6	0,026 4	0,060 8	0,117	0,041 2	0,091 6
Magnetic sector(SHRIMP II)	TEMORA Zircon Standard	207,954	0,038 7	0,045 4	0,030	0,035 4	0,048 1	0,015 6	0,025 5

Table 2 — Mass resolving power($M/\Delta M$) of different definition for M-SIMS and TOF-SIMS

Instrument	Sample	m/z	Mass resolving power ($M/\Delta M$)						
			X % valley		X % peak width			X % peak tail interference	
			10 %	1 %	50 %	10 %	1 %	10 %	1 %
TOF	TEMORA Zircon Standard	207,931	3 100	2 300	7 900	3 400	1 800	5 000	2 300
Magnetic sector(SHRIMP II)	TEMORA Zircon Standard	207,954	5 400	4 600	6 900	5 900	4 300	13 000	8 200

7.2 Mass resolution comparison between TOF-SIMS and FTICR-SIMS

A rat brain tissue section was analysed by FTICR-SIMS (9.0T solariX FT-ICR MS). The same rat brain section was analysed by TOF-SIMS (TRIFT II, Physical Electronics Inc., Chanhassen, MN, USA) with a 22 keV Au^+ primary ions too. Figure 6 shows the spectral overlay of TOF-SIMS (red) and FTICR-SIMS (black) of rat brain section. The high mass resolving power ($M/\Delta M$) of the FTICR-SIMS reveals mass features obscured in the TOF-SIMS spectrum. For comparison, the spectra were scaled to the highest abundance peak in each spectral window. In this example, based on the shape of peak the mass resolving power ($M/\Delta M$) of the FTICR-SIMS is higher regardless of peak separations mentioned in Clause 5. The mass resolving power ($M/\Delta M_{50\,\%}$) of the FTICR-SIMS is about 126,500 at m/z 400, and that of TOF-SIMS is about 1 700 at m/z 371. Table 3 and Table 4 show mass resolution(ΔM) and mass resolving power($M/\Delta M$) for different definition in TOF-SIMS and FTICR-SIMS, respectively.



Key

TOF

FTICR

Figure 6 — Spectral overlay of TOF-SIMS (red) and FTICR-SIMS (black) of the same rat brain section [16]

Table 3 — Mass resolution(ΔM) of different definition for TOF-SIMS and FTICR-SIMS

Instrument	Sample	m/z	Mass resolution (ΔM)						
			X % valley		X % peak width			X % peak tail interference	
			10 %	1 %	50 %	10 %	1 %	10 %	1 %
TOF	Rat brain tissue section	~371			0,215	0,465	0,541	0,209	0,262
FTICR	Rat brain tissue section	~371(400)			0,003 16	0,004 41	0,011 8		

Table 4 — Mass resolving power($M/\Delta M$) of different definition for TOF-SIMS and FTICR-SIMS

Instrument	Sample	m/z	Mass resolving power ($M/\Delta M$)						
			X % valley		X % peak width			X % peak tail interference	
			10 %	1 %	50 %	10 %	1 %	10 %	1 %
TOF	Rat brain tissue section	~371			1 700	800	700	1 800	1 400
FTICR	Rat brain tissue section	~371(400)			126 500	84 100	31 500		

7.3 Mass resolution of flat top mass peak

Mass peaks of SIMS are basically Gaussians or Lorentzians or their mixtures. However, for high precision isotope ratios, flat top peaks are normally needed. Figure 7 shows the flat top mass peak of ^{17}O and ^{16}OH measured by M-SIMS(SHRIMP II). Table 5 and Table 6 shows mass resolution(ΔM) and mass resolving power($M/\Delta M$) for different definition at the flat top mass peak of ^{16}OH.

NOTE On the NanoSIMS (M-SIMS), the separation between two peaks can be increased by inserting a narrower exit slit in front of the detectors. This will increase the mass resolution as defined with 50 % peak width, but be wholly inappropriate for high precision isotope ratio measurements and the slightest drift can result in peak fall off. This also shows that the peak shape should be introduced when describing the mass resolution.

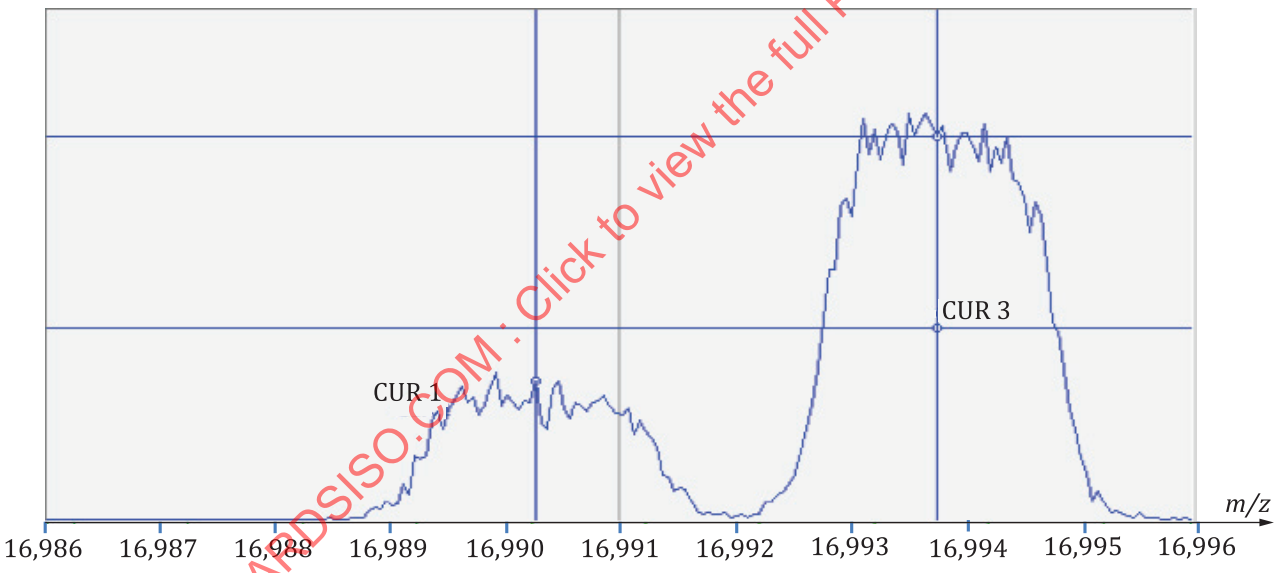


Figure 7 — Flat top mass peak of ^{17}O and ^{16}OH measured by M-SIMS(SHRIMP II) [17]

Table 5 — Mass resolution(ΔM) of different definition for flat top mass peak in M-SIMS

Instrument	Sample	m/z	Mass resolution (ΔM)						
			X % valley		X % peak width			X % peak tail interference	
			10 %	1 %	50 %	10 %	1 %	10 %	1 %
M-SIMS		16,994		0,003 47	0,002 02	0,002 60	0,003 60	0,001 30	0,001 86

Table 6 — Mass resolving power($M/\Delta M$) of different definition for flat top mass peak in M-SIMS

Instrument	Sample	m/z	Mass resolving power ($M/\Delta M$)						
			X % valley		X % peak width			X % peak tail interference	
			10 %	1 %	50 %	10 %	1 %	10 %	1 %
M-SIMS		16,994		4 900	8 400	6 500	4 700	13 100	9 100

8 Conclusion

Based on the discussions and various examples in this document, both peak separation and the peak shape should be included in the definition of mass resolution. For a given peak shape, different types of instruments may use different peak separation to define mass resolution. Furthermore, for similar instruments, according to different analysis purposes, various peak separations have been used to define the mass resolution. Peak separation of 1 % valley is normally used for M-SIMS; peak separation of 50 % peak height (FWHM) is normally used for TOF-SIMS; peak separation of 10 % peak height is normally used for Q-SIMS. In addition, for organic analysis, peak separation of 50 % peak height can be used for TOF-SIMS, but for accurate isotope ratio measurement of geological samples, peak separation of 1 % peak tail interference shall be used. Therefore, beside selecting appropriate peak separation, the analyst need pay attention to the type of instrument used, the properties of the sample and the shape of the mass peak.

Annex A
(informative)

Examples of mass resolution measured by Q-SIMS, TOF-SIMS, Magnetic-SIMS, Orbitrap-SIMS and FTICR-SIMS

A.1 ^{27}Al mass peak measured by Q-SIMS

Figure A.1 shows the ^{27}Al mass peak measured by Q-SIMS based on the X% peak width definition ΔM (X%) or R(X%)=$M/\Delta M$ (X%) for X=10, mass resolution $\Delta M_{10\,\%}$=0,90 m/z, or $M/\Delta M_{10\,\%}$ =30.

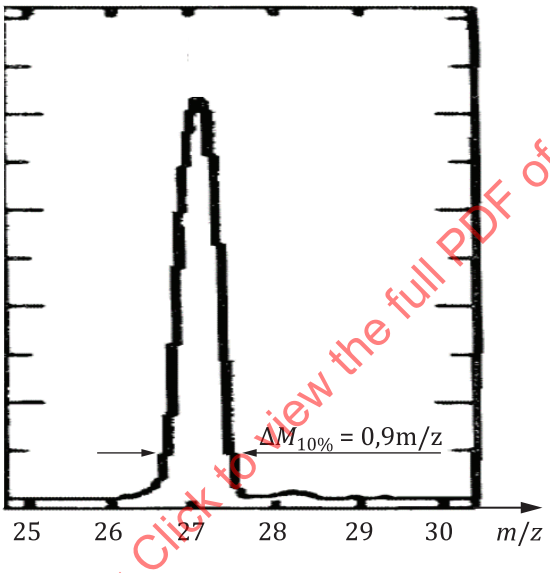


Figure A.1 — ^{27}Al mass peak obtained by Q-SIMS

A.2 ^{28}Si mass peak measured by TOF-SIMS

Figure A.2 shows the ^{28}Si mass peak measured by TOF.SIMS 5 based on the X% peak width definition ΔM (X%) or R(X%)=$M/\Delta M$ (X%) for X=50 (FWHM), mass resolution $\Delta M_{50\,\%}$=0,002 27 m/z, or $M/\Delta M_{50\,\%}$ =12 300.

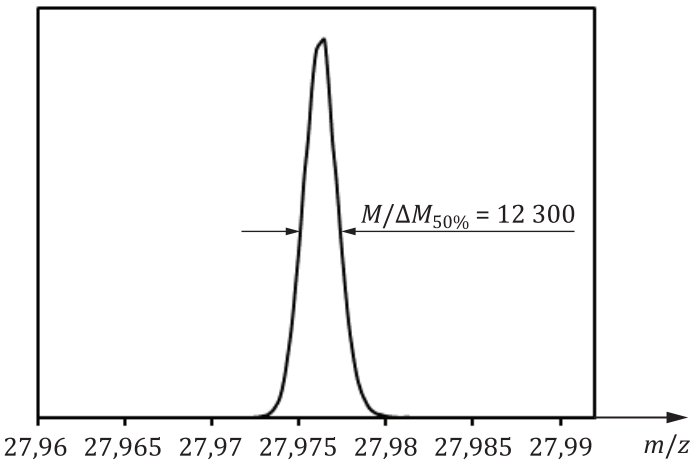


Figure A.2 — ^{28}Si mass peak obtained by TOF.SIMS 5

A.3 ^{28}Si and ^{208}Pb mass peak measured by M-SIMS

Figure A.3 shows the ^{28}Si mass peak measured by Cameca IMS 6f based on the X% peak width definition ΔM (X%) or R(X%)=$M/\Delta M$ (X%) for X=50, mass resolution $\Delta M_{50\,\%}$=0,003 6 m/z, or $M/\Delta M_{50\,\%}$ =7 700. For X=1, $\Delta M_{1\,\%}$=0,008 6 m/z, $M/\Delta M_{1\,\%}$=3 300.

Figure A.4 shows the ^{208}Pb mass peak measured by SHRIMP II based on the X% peak valley definition ΔM (X%) or R(X%)=$M/\Delta M$ (X%) for X=1, mass resolution $\Delta M_{1\,\%}$=0,045 m/z, or $M/\Delta M_{1\,\%}$ =4 600. If based on X% peak width definition, $\Delta M_{1\,\%}$=0,048 m/z, $M/\Delta M_{1\,\%}$=4 300,For X=50, $\Delta M_{50\,\%}$=0,030 m/z, $M/\Delta M_{50\,\%}$=6 900.

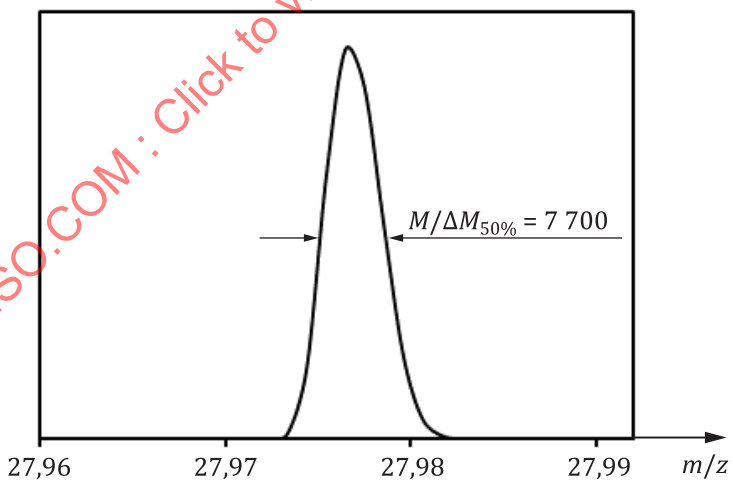


Figure A.3 — ^{28}Si mass peak obtained by Cameca IMS 6f