MS Tips No.43 Analysis of Impurities in Ethylene glycols with JMS-T100GC AccuTOF GC

The JMS-T100GC AccuTOF GC, featuring high resolution and high sensitivity, can be utilized in qualitative analysis of ultra trace components. We analyzed impurities in three commercial reagents, ethylene glycol, diethylene glycol, and triethylene glycol, by using EI and CI. The method is as follows.

Conditions

Sample		Ethylene glycol, diethylene glycol, triethylene glycol
GC	Injection method	Split (1:200)
	Injection volume	1.0 µL
	Column	DB-5 ms, ID 0.25 mm × Length 30 m, film thickness 0.25 µm
	Oven program	80℃(2 min)→ 20℃/min → 280℃(2 min)

Results

Analytical results are shown below. Figure 1 shows, from the top, the TIC data of ethylene glycol, diethylene glycol, and triethylene glycol. The commercial reagents were analyzed without modification. The results showed impurities in each sample. Since the reagents were purchased a few years ago, the impurities detected were divided into two types: original components and decomposition products.

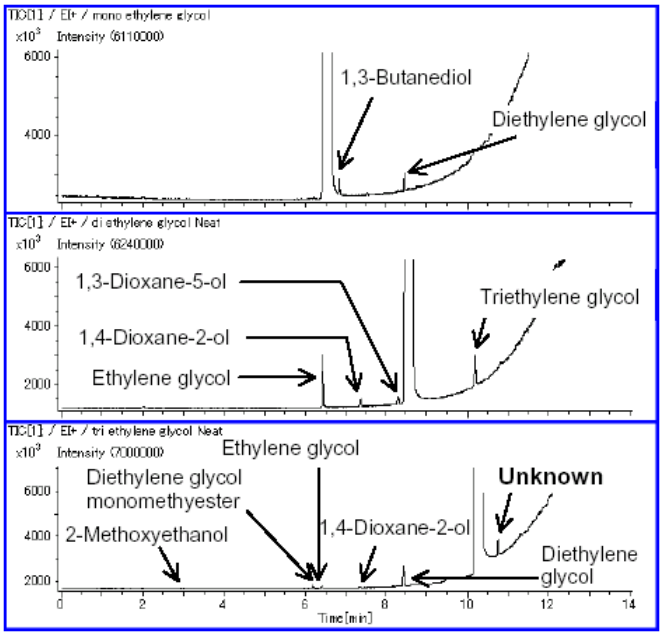


Figure 1. TIC of target samples

Table 1 shows the components identified from database search and their ratio calculated from the TIC chromatogram peak area.

Sample	Component detected	Area	Ratio (%)

Ethylene glycol	Ethylene glycol	2605987	99.21
	1,3-Butanediol	7782	0.30
	Diethylene glycol	12877	0.49
Diethylene glycol	Diethylene glycol	3499352	96.93
	Ethylene glycol	62758	1.74
	1,4-Dioxane-2-ol	7928	0.22
	1.3-Dioxane-5-ol	7763	0.21
	Triethylene glycol	32529	0.90
Triethylene glycol	Triethylene glycol	3903639	98.47
	2-Methoxyethanol	1958	0.05
	Diethylene glycol monomethylester	5470	0.14
	Ethylene glycol	3829	0.10
	1,4-Dioxane-2-ol	2487	0.06
	Diethylene glycol	24671	0.70
	Unknown	19174	0.48

Table 1. Components in samples

Since we were unable to identify the unknown component in triethylene glycol through NIST library database search, we obtained elemental compositions from the exact masses of the ions detected in EI and CI (ammonia as reagent gas), estimating the composition of the unknown. Results are shown below.

Ionization	Measured	Theoretical	Error (mmu)	Composition	Unsaturation
CI	210.13355	210.13415	-0.60	$C_8H_{20}NO_5$	-0.5
	193.10588	193.10760	-1.72	$C_8H_{17}O_5$	0.5
	124.09866	124.09737	1.30	$C_4H_{14}NO_3$	-1.5
	107.07068	107.07082	-0.14	$C_4H_{11}O_3$	-0.5
EI	104.04713	104.04734	-0.22	$C_4H_8O_3$	1.0
	87.04436	87.04460	-0.24	$C_4H_7O_2$	1.5
	73.02895	73.02895	0.00	$C_3H_5O_2$	1.5
	45.03455	45.03404	0.51	C_2H_5O	0.5
	31.01871	31.01839	0.32	CH_3O	0.5

Table 2. Elemental composition of unknown component in triethylene glycol

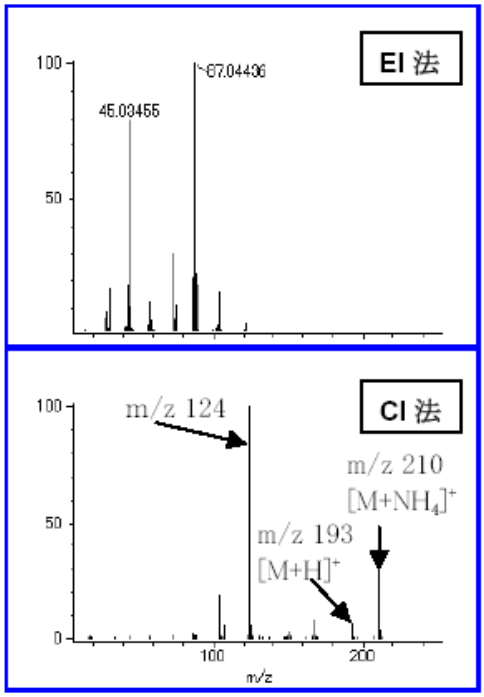


Figure 2. Mass spectra of unknown component in triethylene glycol

The results suggest that m/z 124 detected as the base peak in CI is [$C_4H_{14}NO_3$]$^+$. However, since peaks with relatively high intensity were detected at higher m/z, m/z 124 is not a molecular ion. Thus, m/z 210 and m/z 193 are likely to be $[M+NH_4]^+$ and $[M+H]^+$ respectively, and the exact mass suggests that the unknown component has a composition of $C_8H_{16}O_5$.Furthermore, the composition of the fragment ions detected in EI suggest that the unknown component is the ester compound shown in Figure 3.

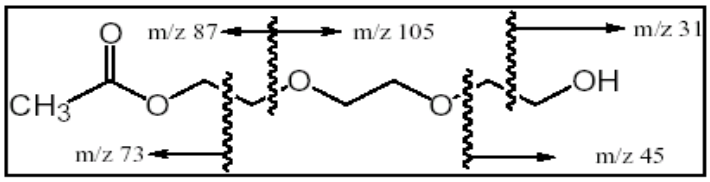


Figure 3. Estimated structure of unknown component in triethylene glycol

Summary

The JMS-T100GC AccuTOF GC is characterized by its high mass accuracy. Thus, the AccuTOF GC performs exact mass measurement with a single ion as internal reference. Because the AccuTOF GC can obtain exact masses in CI, which is traditionally a difficult experiment, the system is a powerful tool for structural and qualitative analysis of target components.

MS Tips No.39 JMS-T100GC AccuTOF GC: Analysis of Aroma Chemicals with Fast GC/MS

Fast GC is attracting increasing attention. Fast GC uses narrow, short columns, approximately 0.1 mm ID and 10 m long, to speed up the separation process while maintaining the high resolution equal to conventional GC. Fast GC, when combined with mass spectrometry, results in a high throughput GC/MS system. Presently, TOFMS is the only mass spectrometer that meets the speed of spectrum recording needed for fast GC, in which the FWHM of chromatogram peaks is much smaller. Existing GC-TOFMS systems, however, either do not have the capability of exact mass measurement or do not support fast GC because of the low data acquisition rate.
JEOL's JMS-T100GC AccuTOF GC is a new type of GC-TOFMS combining the speed compatible to fast GC/MS, ease of operation, and exact-mass measurement capability. We have analyzed the same sample in the JMS-T100GC AccuTOF GC using conventional GC/MS and fast GC/MS, and compared the results.

Conditions

	GC/MS	Fast GC/MS
Sample	Lavender oil	
Injection method	Split (1:500)	
Injection volume	0.2 µL	
Column	DB-5ms: ID 0.25 mm × Length 30 m, film thickness 0.25 µm	BPX-5: ID 0.1mm × Length 10m, film thickness 0.1 µm
Oven program	70°C (0.5 min) →10°C/min→250°C (3 min)	70°C (0.5 min) →60°C/min→250°C (3 min)
Mass range	m/z 35 to 300	
Recording speed	0.2 sec (5 spectra/sec)	0.04 sec (25 spectra/sec)

Results

For fast GC we used a short, narrow column,10 m long and 0.1 mm ID, and increased the oven temperature rapidly at 60°C/min. If a conventional column, DB-5ms (30 m long and 0.25 mm ID), is used at the same oven temperature as fast GC, peaks detected will not be fully separated. To speed up the separation, the oven temperature has to increase more quickly to separate the components. To maintain the high resolution during the rapid oven temperature ramp, shorter and narrower GC columns are necessary.
Figure 1 shows the total ion chromatograms obtained in conventional GC/MS (12 min) and fast GC/MS (3 min). Fast GC completed the separation in 3 minutes, 1/4 of conventional GC. With the time

needed for preparation and data processing excluded, fast GC increased the throughput of the experiment 4 times compared to GC.

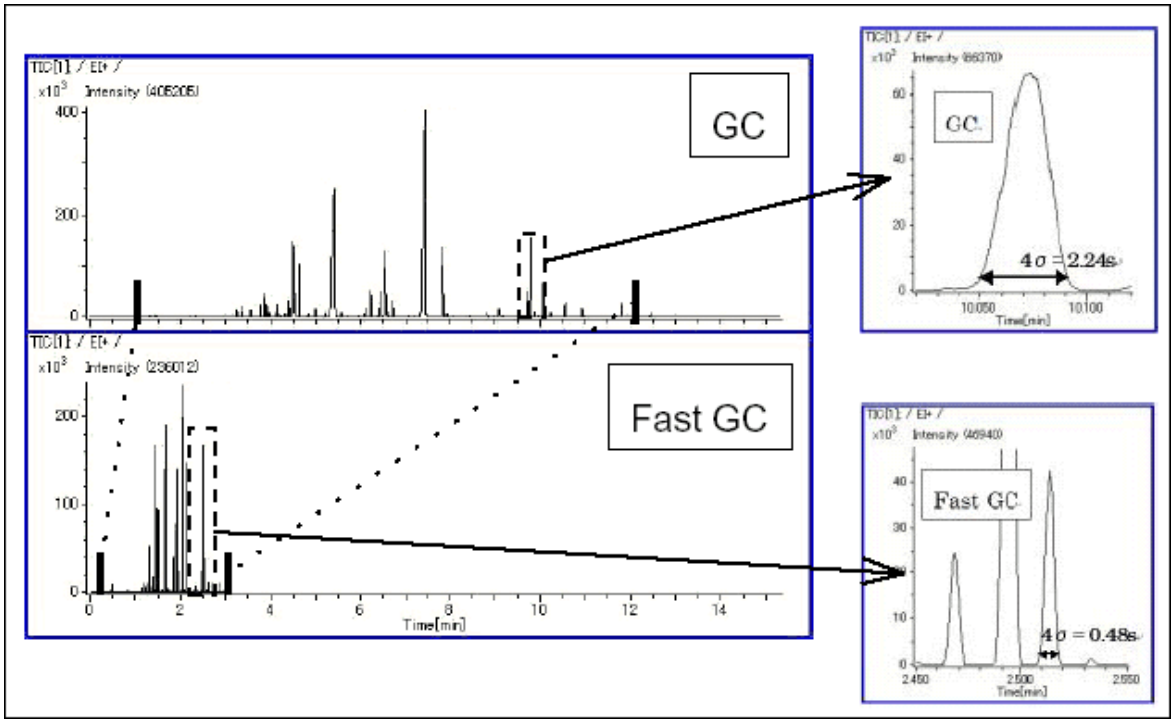


Figure 1. GC and Fast GC: Analytical results and chromatogram peaks of B-Farnesene

Fast GC, using narrower, shorter columns, results in a chromatogram peak width of 0.5 to 1 sec compared to 2 to 3 sec in conventional GC. QMS, widely used as GC-MS and field MS for environmental studies and having a maximum recording speed (scan speed) of 0.2 to 0.4 sec, is not effective in fast GC, failing to acquire sufficient data points per peak (see Figure 2 left). The JMS-T100GC AccuTOF GC, capable of acquiring the mass spectrum of the entire range in 0.04 sec at maximum (25 spectra/sec), can be combined with fast GC to maintain high resolution of chromatogram (Figure 2 right).

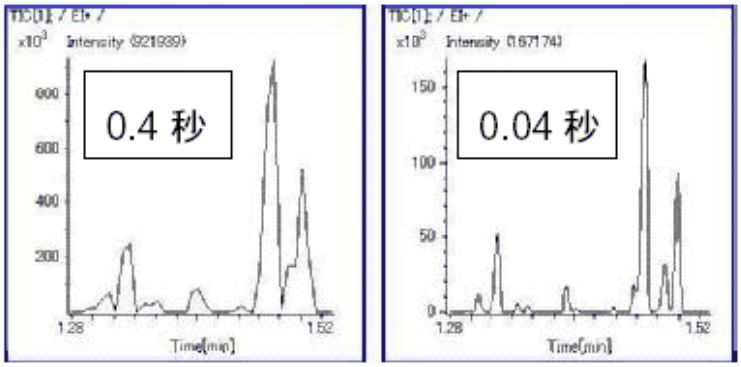


Figure 2. Chromatogram peak analysis in fast GC at different recording speeds (Left: 0.4 sec; right: 0.04 sec; both acquired in AccTOF GC)

Summary

Fast GC/MS is an effective technique in increasing the throughput for total GC-MS analysis.

Conventional field MS and QMS fail to support fast GC/MS because of the high recording speed needed. The JMS-T100GC AccuTOF GC can be effectively combined with fast GC. Its high mass spectrum recording speed up to 0.04 sec, ease of operation, exact-mass measurement capability, and stable high resolution make it a powerful high throughput GC/MS system.

MS Tips No.40 Identification of Liquid Crystal Components in JMS-T100GC AccuTOF GC with Exact-Mass Measurement

Gas chromatograph mass spectrometry (GC-MS) is a powerful analytical technique for qualitative and quantitative analysis of organic compounds with relatively low boiling points. Gas chromatography separates the sample into components, while mass spectrometry acquires mass spectral data of the components for qualitative analysis. Ion intensities of the components are further used for quantitative analysis.

Qualitative analysis in GC-MS compares spectral data acquired from a sample with known spectra in a library database to identify the components. For unknown components not contained in the library database, fragment ions are used to study their possible chemical structure. Integral masses alone, however, are often not enough for successful structural analysis. In such cases, exact masses of the ions are used to estimate the composition and structure.

We have identified an unknown component in liquid crystal with JEOL's JMS-T100GC AccuTOF GC by using exact masses of the ions obtained in EI and CI. An outline of our experiment is as follows.

Conditions

Sample	Sample	Liquid crystal from a commercial calculator dissolved in hexan
	Mass calibration sample	2,4,6-Tris (trifluoromethyl) -1,3,5-triazine (TTT)
CI gas		Isobutene (0.1 mL/min)

GC	Injection method	Split (1: 400 for EI; 1: 200 for CI)
	Injection volume	1.0 µL
	Column	DB-5, 0.18 mm (IO) × 10 m (L), film thickness 0.18 µm
	Oven program	40°C (1 min) → 50°C/min → 300°C (1 min)

Results

Figure 1 shows peaks obtained in EI and CI, where the sample was introduced by split injection. We focused on the first peak detected at a retention time of around 5.0 min (Component A).Figure 2 shows mass spectra of unknown Component A in the liquid crystal sample obtained in EI and CI. When Component A was analyzed in EI, the base peak was detected at m/z 111, followed by ions at m/z 69 and m/z 195.In CI, the base peak was detected at m/z 334. EI detected a small ion peak at m/z 333 as well, suggesting that the ion at m/z 333 is the molecular ion of Component A. However, the mass spectrum obtained in EI did not match with any compound in the NIST library database. Even the spectral pattern of the primary candidate (Match 557) did not match, whose molecular weight was not 333.

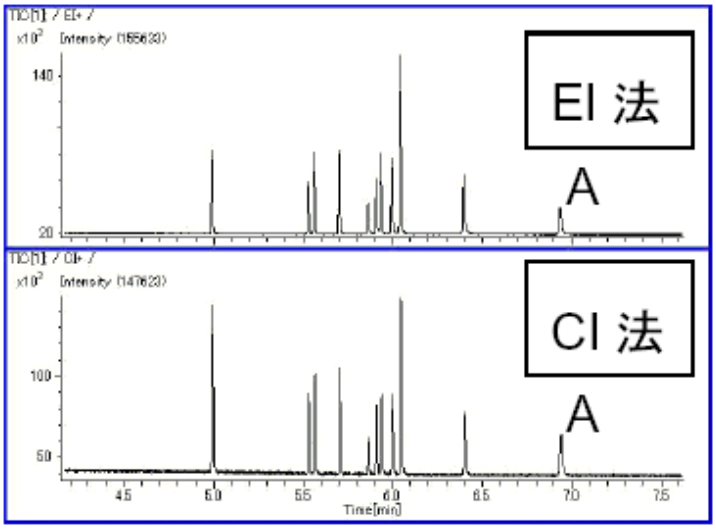


Figure 1. TIC of liquid crystal (top: EI; bottom: CI)

None of the other candidates had a molecular weight of 333, suggesting that the component is unlikely to be present in the NIST library database. Thus, we calculated exact masses of the ions to estimate the composition.

Since the molecular weight is an odd number of 333, it is expected that the component contains an odd number of nitrogen atoms based on the Nitrogen Rule. For estimating, we made a guess for elements and their quantities based on the typical liquid crystal congeners.[1] Table 1 illustrates the results estimated from the exact mass of m/z 334 in the mass spectrum obtained in CI. The error was set within 2 mmu in calculating the estimation results. Typical components in the liquid crystal congeners containing 3 oxygen atoms are either azoxy compounds or p-cyanophenyl esters in p-alkyl substituted benzoic acid. None of these compounds, however, is reported to contain fluoric atoms. This suggests that (1) is the more likely composition. We estimated the structure from ($C_{22}H_{24}NO_2$) in (1) and the fragment pattern obtained in EI. Table 2 shows the estimation results of the ions detected in EI.

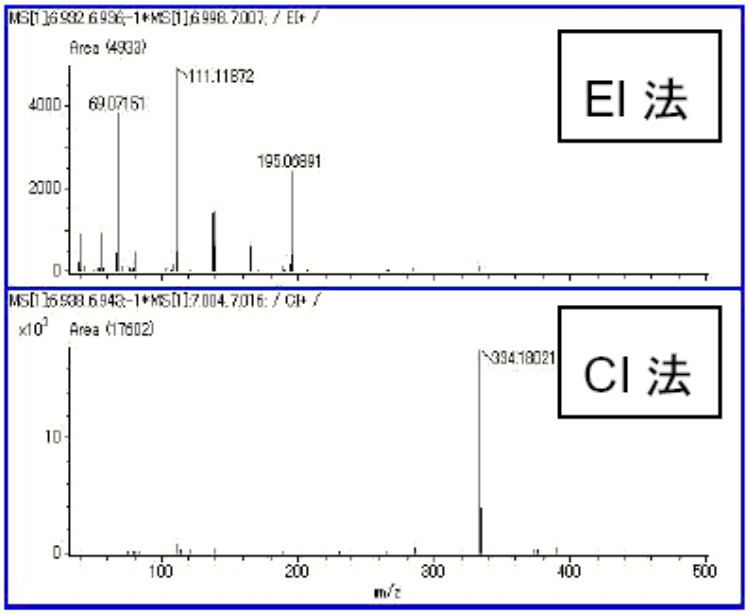


Figure 2. Mass spectra of Component A

	Measured	Theoretical	Error (mmu)	Estimated composition	Unsaturation
(1)	334.18021	334.18070	-0.49	$C_{22}H_{24}NO_2$	11.5
(2)		334.18185	-1.64	$C_{19}H_{25}FNO_3$	7.5

Table 1. Estimation results of $[M+H]^+$ of Component A detected in CI

Ion (m/z)	Measured	Theoretical	Error (mmu)	Estimated composition	Unsaturation
333	333.17432	333.17288	1.44	$C_{22}H_{23}NO_2$	12
195	195.06891	195.06841	0.5	$C_{13}H_9NO$	10
111	111.11872	111.11738	1.34	C_8H_{15}	1.5
69	69.07151	69.07042	1.09	C_5H_9	1.5

Table 2. Estimation results of ions of Component A detected in EI

Composition (1) in Table 1 contains one nitrogen atom. This must be part of the cyano group (-CN) because there are no known compounds among the liquid crystal congeners containing amino ($-NH_2$) or nitro ($-NO_2$) group. Two oxygen atoms in (1) suggest an ester group. Furthermore, an unsaturation number of 12 for $[M]^+$ in Table 2 suggests that one or two benzene rings are contained. These suggestions directed us to two possible structures shown in Figure 3: p-cyanophenyl ester and aryl ester substituted cyclohexane carboxylic acid.

We assumed that the m/z 111 ion resulted from a simple split of the alkyl group while the m/z/ 69 ion from a hydrogen transfer within the cyclohexane ring. These ions can be generated from either [I] or [II].On the other hand, the m/z 195 ion is unlikely to have been generated from [II] due to its structure. It resulted from [I] by a simple split of the alalkoxy group accompanied by a hydrogen transfer. Therefore,

the fragment ions detected in EI suggest that Component A has the structure of [I] in Figure 3.

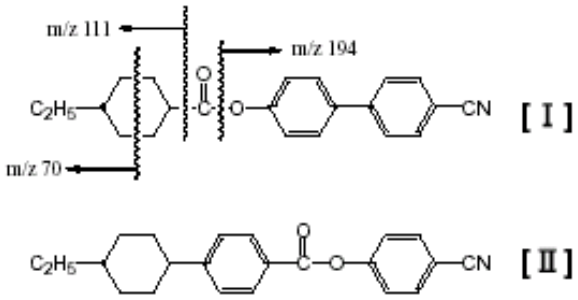


Figure 3. Estimated structure of Component A

Summary

The JMS-T100GC AccuTOF GC detects ions with high mass accuracy. The combination of EI and CI mass spectra obtained with exact mass measurement makes the system a powerful tool for structural and qualitative analysis of target components.

Reference

[1] Dictionary of Liquid Crystals compiled by Liquid Crystal Section, Committee 142 for Organic Materials for Information Science, Japan Society for the Promotion of Science, published by Baifukan.

MS Tips No.35 Cold-Spray TOFMS: Effect of Retractable Flow Redirector

In general LC-MS, ESI is known to be effective for analysis of ionic or polar compounds as the softest ionization method. However, it is extremely difficult for ESI to identify the structure of labile organic compounds in solution. Cold-spray ionization[1)] is a new technique recently developed to solve this problem.

Cold-spray ionization, reported by Dr. Kentaro Yamaguchi, Tokushima Bunri University, is designed to ionize samples at low temperature by cooling nitrogen gas spray. Ions generated by this technique are likely to be ionized while maintaining the associative structure reflecting the inherent properties of molecules. Studying these ions will enable general structural analysis including molecular functions and peripheral environment.

In 2003 JEOL announced the JMS-T100CS AccuTOF CS, incorporating a new ion source designed to support cold-spray ionization. The new ion source features a retractable flow redirector designed to switch the direction of spray between vertical and coaxial. We analyzed proline in an AccuTOF CS, studying the effect of the retractable flow redirector.

AccuTOF CS: System Overview

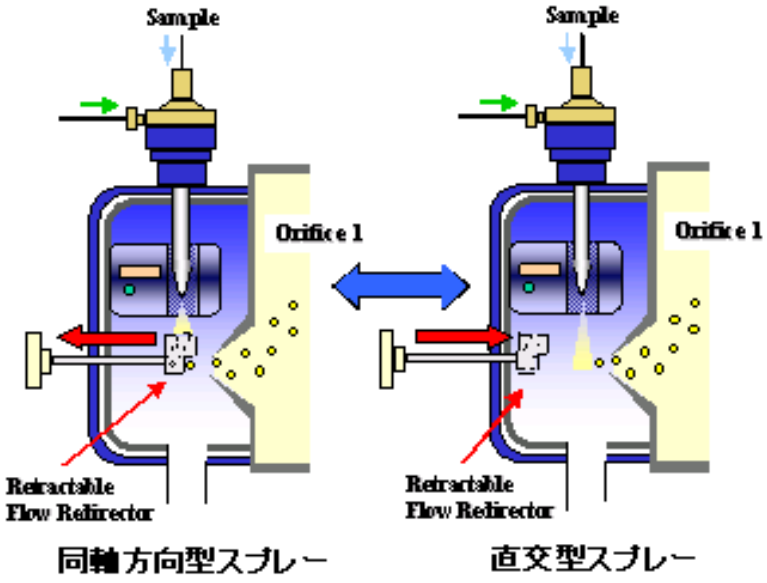
- Features of AccuTOF -

The AccuTOF CS, keeping the same levels of spectral sensitivity, mass accuracy, and wide dynamic range as the AccuTOF, has an additional advantage of easy maintenance.

The isolation valve on top of the MS system allows the ion source/injector and the analyzer/detector to independently control evacuation.

This design substantially enhanced the speed and minimized the labor required for daily maintenance.

- Retractable Flow Redirector -



Vertical gas flows from the sprayer are effective in minimizing contamination buildup in the MS system. For some samples, however, ionization efficiency is often inferior to coaxial gas flows.

Thus, the ion source integrates a retractable flow director controlling gas flows from the sprayer in vertical and coaxial directions.

Analysis of proline

- Objective -

We analyzed proline, a cyclic amino acid, using cold-spray ionization. We used the retractable flow redirector to acquire data with vertical and coaxial gas flows, identified cluster ions from the mass spectra, and studied the effect of the retractable flow redirector.

The temperature at the tip of the sprayer during the experiment was 0 to 10 degrees.

Acquisition Conditions (L-proline)	
Sample introduction	Infusion with syringe pump
Flow rate	1.0 ml/hr
Ionization	Cold-spray
Coolant	Liquid nitrogen
Desolvating temperature control	OFF
Orifice 1 temperature control	OFF
Nebulizing gas	N_2 (0.75 L/min)
Drying gas	OFF
Needle voltage	0 V and 2000 V
Ring lens voltage	20 V

Orifice 1 voltage	100 V
Orifice 2 voltage	5 V
Ion guide voltage	2500 V
Detector voltage	2800 V
Mass range	m/z 200 to 5000
Experiment time:	3 min
Recording interval	10 sec

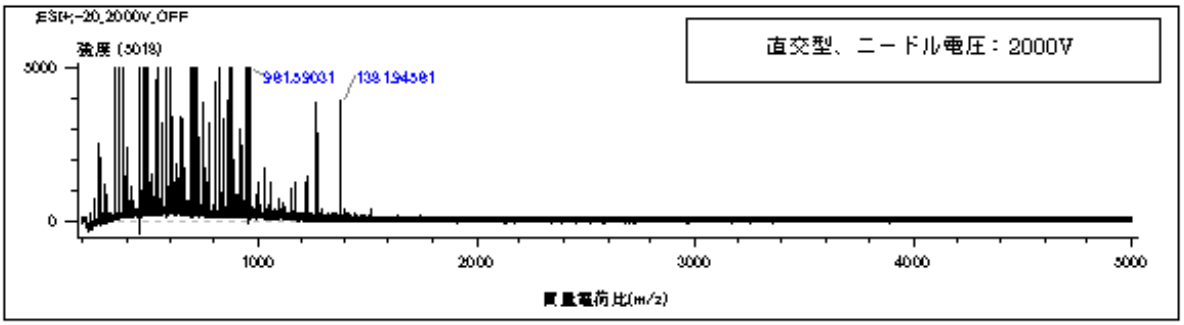
- Results -

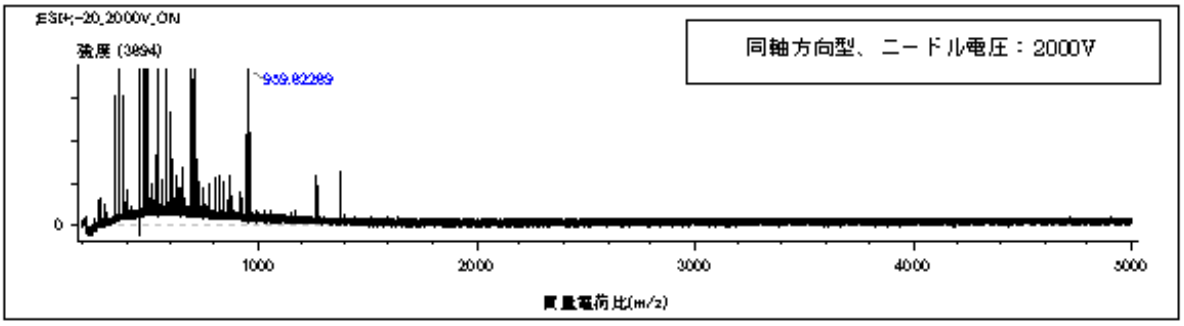
With the vertical gas flow, no cluster ions were detected when the needle voltage was set to 2000 V and 0 V.

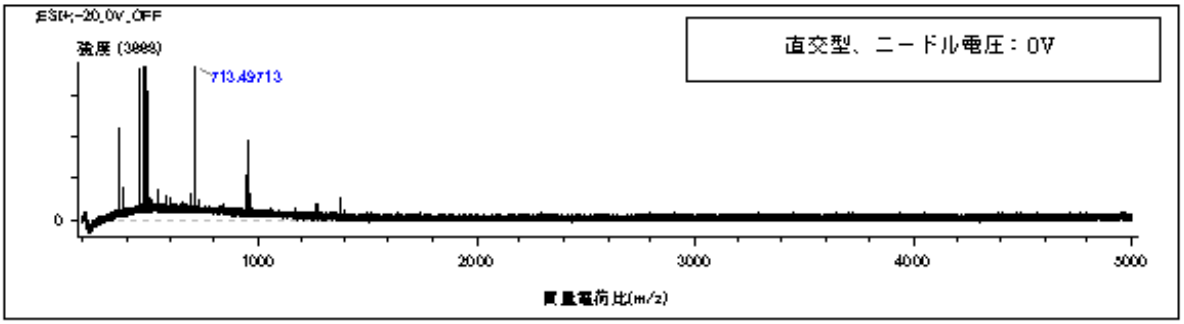
On the other hand, with the coaxial gas flow, cluster ions were detected in a mass range up to 5000 Da when the needle voltage was 0 V, although no cluster ions were detected when the needle voltage was 2000 V. The system detected single charged ions of up to 43 in the proline multimer.

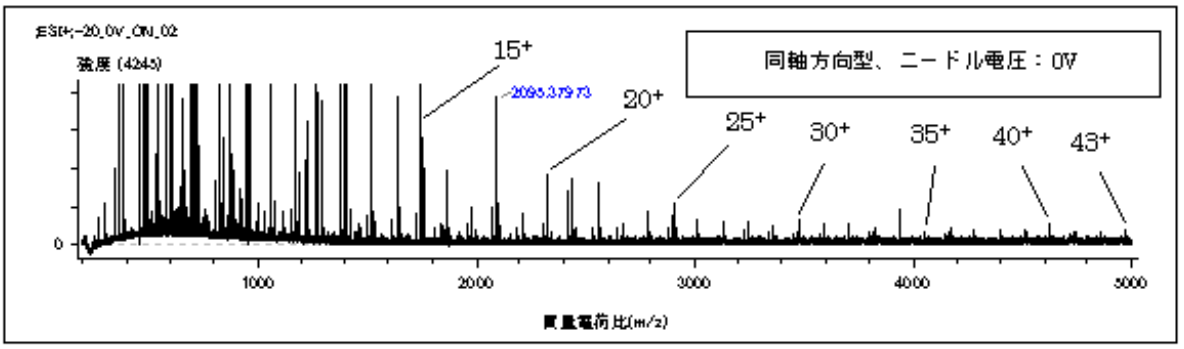
The results demonstrate that cold-spray ionization is extremely effective in identifying biomolecular clusters composed of a relatively weak hydrogen bond such as proline. The retractable flow redirector was also effective in such analysis.

When using cold-spray ionization on biomolecules, the direction of the gas flow should be selected according to the sample analyzed.









[Reference]

1) K.Yamaguchi : Cold-spray ionization mass spectrometry: principle and applications, Journal of mass spectrometry, 2003, 38, 473-490

MS Tips No.37 CE-TOFMS in JMS-T100LC: Analysis of a Cold Medicine

JEOL's LC-TOFMS JMS-T100LC AccuTOF supports capillary electrophoresis (CE) through a triple tube sprayer.[1)] We analyzed an over-the-counter cold medicine using CE-TOFMS in the AccuTOF.

Conditions

Mass spectrometer	JMS-T100LC
CE	Agilent capillary electrophoresis system (Agilent Technologies)

CE conditions	
Buffer	1M CH_3COOH (pH: 2.4)
Sheath	1% CH_3COOH-H_2O/CH_3OH=50/50 (10 μL/min)
Injection	50 mbar × 4 sec (approx. 4 nL)
Capillary	Fused silica (ID 50 μm, 80 cm long)
CE voltage	30 kV

MS Conditions	
Ionization	ESI+
Nebulizing gas	N_2 (1 L/min)
Drying gas	OFF
Desolvation chamber temperature	250°C
Orifice 1 temperature	80°C
Ion guide voltage	700 V
Mass range	m/z 100 to 500
Needle voltage	2500 V
Ring lens voltage	13 V
Orifice 1 voltage	35 V
Orifice 2 voltage	8 V

Detector voltage	2600 V

Results

An over-the-counter cold medicine was dissolved in water and passed through a 0.5 µm filter. Figure 1 shows mass electropherograms of major ingredients of the cold medicine. The 6 ingredients listed on the package were detected with high sensitivity. Figure 2 shows mass spectra of the ingredients. Chlorpheniramine maleate, methylephedrine hydrochloride, and dihydrocodeine phosphate were detected as free $[M+H]^+$ with maleic acid, hydrochloric acid, and phosphoric acid removed respectively, while $[M+H]^+$ ions were detected as the main peak for the other ingredients.

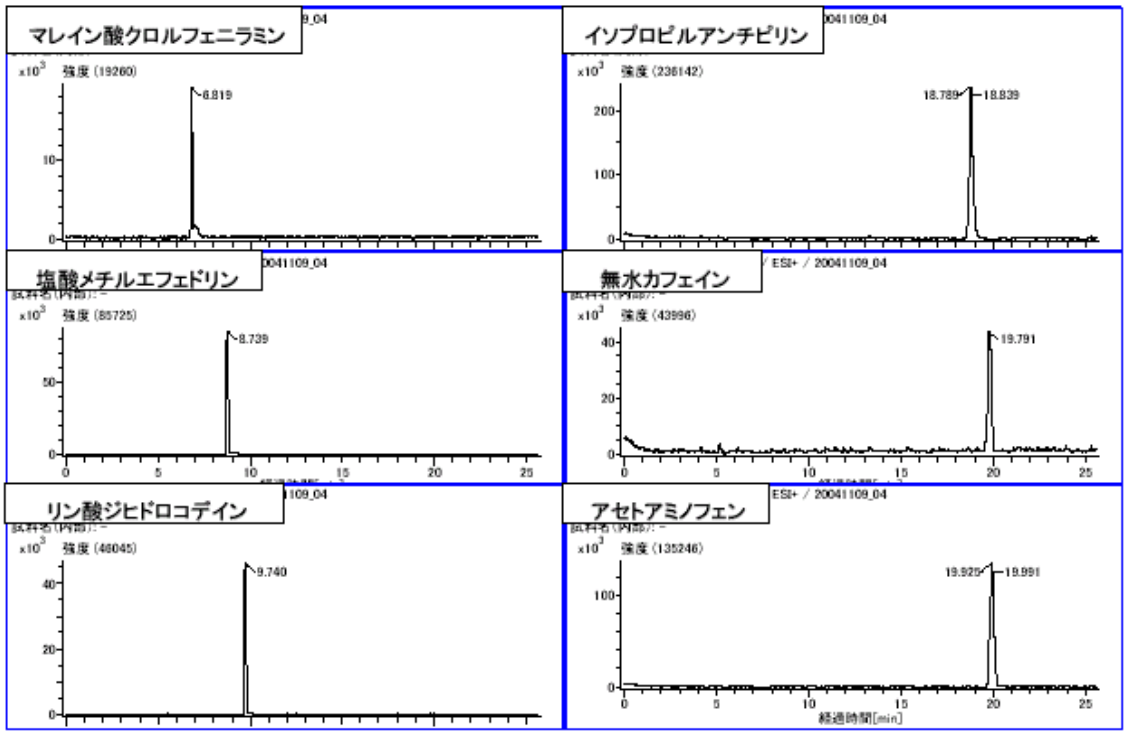


Figure 1. Mass electropherograms of 6 ingredients of cold medicine

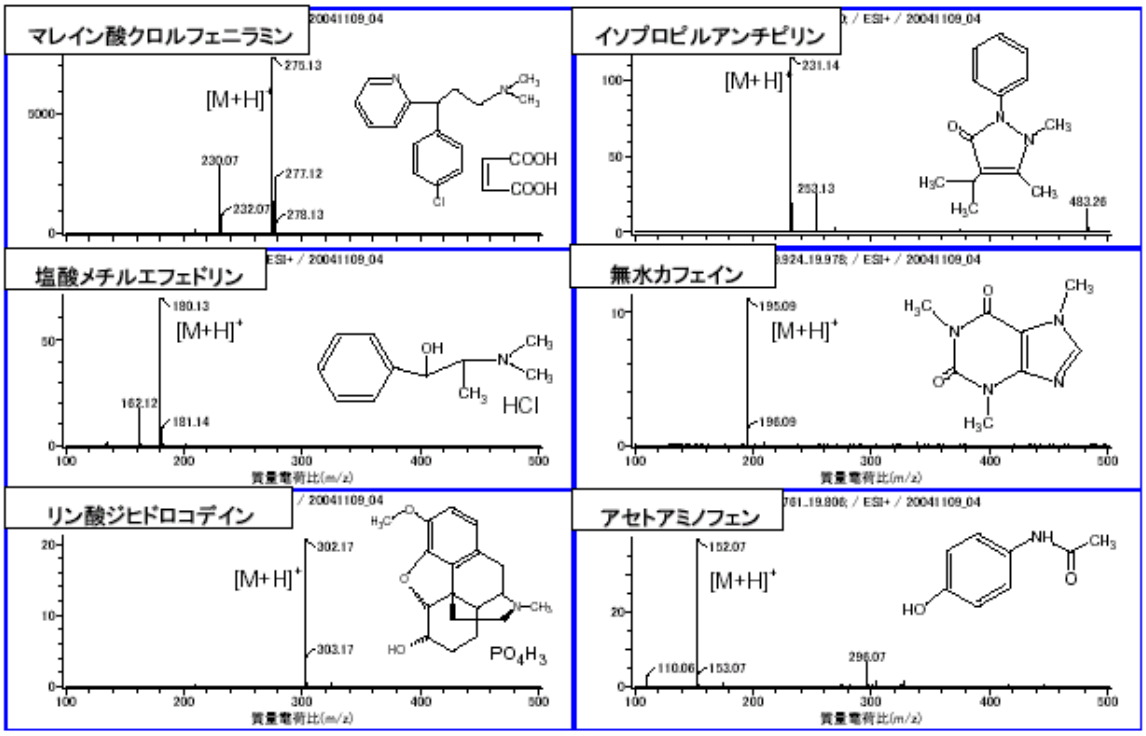


Figure 2. Mass spectra of cold medicine ingredients

Summary

CE-TOFMS enabled speedy analysis of the over-the-counter cold medicine with little preliminary preparation. The volume of the sample needed was extremely small, demonstrating high sensitivity of the system.

Reference

1) MS Tips No. 17 CE-MS Interface: Triple Tube Sprayer

MS Tips No. 47 AP MALDI Ion Source: Analysis of Phosphorylated Peptide

Atmospheric pressure matrix-assisted laser desorption/ionization (AP MALDI) is a technique designed for soft ionization of samples in atmosphere. JEOL's LC-TOFMS JMS-T100LP AccuTOF LC-plus supports an AP MALDI ion source. The system, connected to an AP MALDI ion source, has the following advantages over MALDI-TOFMS, a conventional ionization technique in vacuum, or existing AP MALDI-ITMS (ion trap mass spectrometry).

- Softer ionization than MALDI enables analysis of compounds having weak bonding such as sulfated and phosphorylated peptides.
- A single analyzer can accommodate ESI, APCI, and MALDI ion sources.
- High mass accuracy analysis (up to 3 ppm) regardless of the crystalline condition
- High throughput analysis when combined with a laser with a pulse pitch of 100 Hz or higher

We will introduce data acquired in AP MALDI- TOFMS.

System Configuration

Figure 1 shows an external view of an AP MALDI-TOFMS and a schematic view of its ion source. The ion source is a Mass Tech Model 611 AP/MALDI.
A nitrogen laser beam with a wavelength of 337 mm and a frequency of 10 Hz is forwarded through an optical fiber to the ion source, where it is focused by a lens onto a sample plate. The sample plate has 96 spots (12x8), each of which can be viewed by a CCD camera and monitor. Positioning of the laser is computer-controlled. A voltage of 2 to 4 kV is constantly applied to the sample plate, and resulting ions are introduced to a stainless steel capillary. A heater heats the capillary up to 400°C, efficiently directing the ions from atmosphere to high vacuum.
The ion source, in atmosphere, allows for speedy loading and unloading of the sample plate. The ion

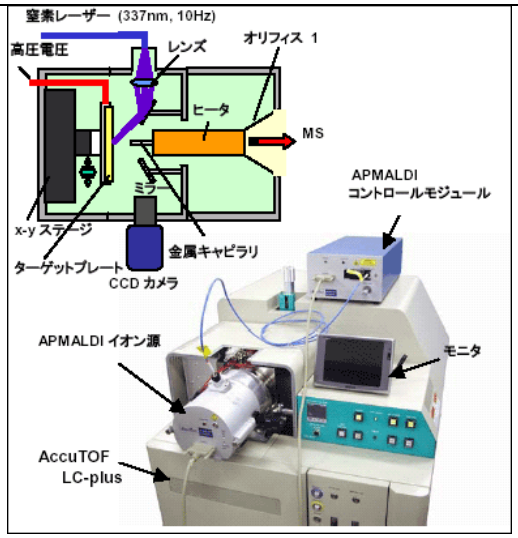


Figure 1. Schematic view of ion source and external view of AP MALDI-TOFMS

source can be changed to another API ion source (ESI, APCI).

Sample Preparation

The sample was prepared in the same way as conventional MALDI. The sample-matrix mixed solution (volume 1 uL) was spotted on a target plate, and was crystallized naturally. The matrix was α-cyamo-4-hydroxycinnamic acid.

Results

β-casein (bovine) fragment 1-25, which has 4 phosphorylated serines from post translational modification, was analyzed. Figure 2 shows the mass spectra acquired in AP MALDI-TOFMS and conventional MALDI-TOFMS with Linear and Reflectron modes. The molecular ion peak of phosphorylated peptide, not detected in the Reflectron mode of MALDI-TOFMS (C), was clearly detected in AP MALDI-TOFMS (A) and in the Linear mode of MALDI-TOFMS (B).

In conventional MALDI, phosphorylated peptide was fragmented due to post source decay (PSD). As a result, no parent ion was observed in the high resolution Reflectron mode. In the low resolution Linear mode, the fragment ions generated by PSD were forwarded to the detector at the same speed as the parent ion, and detected as parent ions. In AP MALDI-TOFMS, because of its soft ionization, phosphorylated peptide was forwarded to the detector without being fragmented, resulting in a high resolution spectrum of the parent ion.

AP MALDI-TOFMS, designed for soft ionization, is capable of detecting molecular ions at high resolution whereas conventional MALDI, where ions are likely to fragment, can only detect molecular ions in the Linear mode at low resolution. AP MALDI-TOFMS is effective for high resolution, high mass accuracy analysis of compounds with weak bonding.

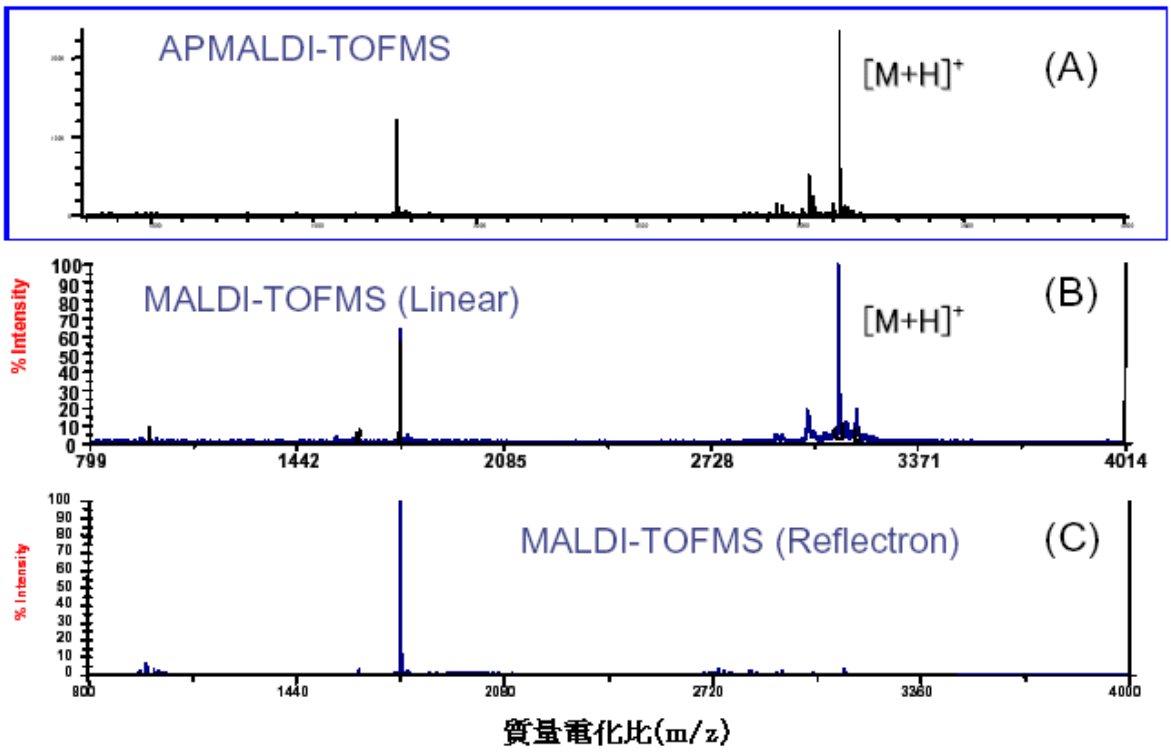


Figure 2. MS spectra of β-casein （bovine）fragment 1-25 acquired in AP MALDI-TOFMS (A), Linear mode of MALDI (B), and Reflectron mode of MALDI (C)

Summary

AP MALDI-TOFMS is capable of analysis of peptide having weak bonding resulting from post translational modification at high mass accuracy. It is a technique effective for proteome analysis to identify proteins from digested proteins by peptide mass fingerprint (PMF).

Acknowledgement

β-casein （bovine）fragment 1-25: Courtesy of Dr. Toshifumi Takao, Proteomics Center, Institute of Protein Research, Osaka University

MS Tips No.46 CE-TOF in JMS-T100LP AccuTOF LC-plus: Analysis of Anions in Plating Liquid

We have analyzed anions in plating liquid using CE-TOFMS in the JMS-T100LP AccuTOF LC-plus combined with capillary electrophoresis.

Conditions

Mass spectrometer	JMS-T100LP AccuTOF LC-plus
CE	Agilent capillary electrophoresis system (Agilent Technologies)
Sample	Two plating liquids (diluted 100 times with ultra pure water) (1) Electroless nickel plating liquid (2) Gloss nickel plating liquid

CE conditions	
Buffer	50mM CH_3COONH_4 (pH: 5.7)
Sheath	5mM NH_4-H_2O/CH_3OH=75/25 (5 μL/min)
Injection	50 mbar × 4 sec (approx. 4 nL)
Capillary	Smile (+) (ID 50 μm, 90 cm long, Nacalai Tesque)
CE voltage	-25 kV

MS Conditions			
Ionization	ESI-	Measurement range	m/z 10 to 300
Nebulizing gas	N_2 (2 L/min)	Needle voltage	3000 V
Drying gas	OFF	Ring lens voltage	10 V
Desolvation chamber temperature	250°□	Orifice 1 voltage	30 to 60 V (sweep)

Orifice 1 temperature	80°C	Orifice 2 voltage	5 V
Ion guide voltage	100 V	Detector voltage	2800 V

Results

Two plating liquids were diluted 100 times with ultra pure water and passed through a 5-µm filter. Figure 1 shows accumulated mass electropherograms of anions detected from the two plating liquid samples. From Sample (1), three organic acids (malate, succinate, and lactate) and 3 inorganic anions (HSO_4^-, $H_2PO_2^-$, and $H_2PO_3^-$) were detected. From Sample (2), only the HSO_4^- ion was detected. Figure 2 is the mass spectra of the 6 anions detected from Sample (1). Organic acids and inorganic anions were detected as $[M-H]^-$ and $[M]^-$ ions respectively.

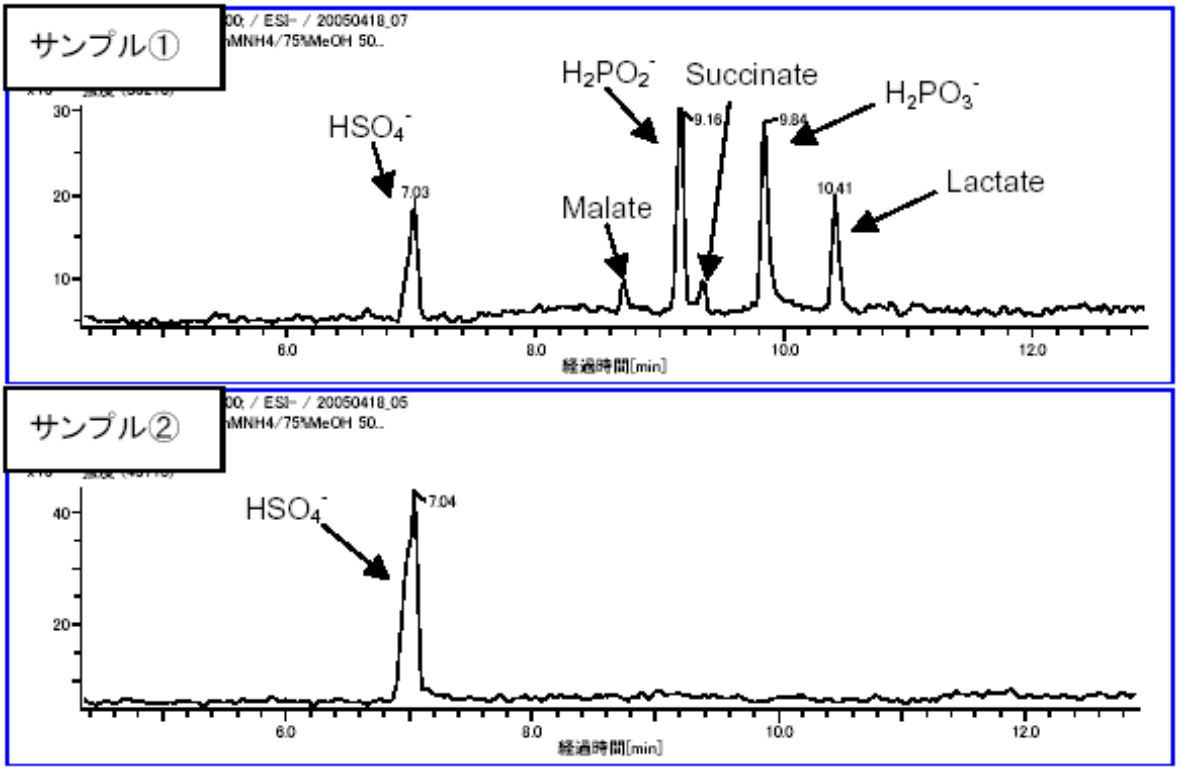


Figure 1. Mass electropherograms of anions in plating liquids (accumulated)

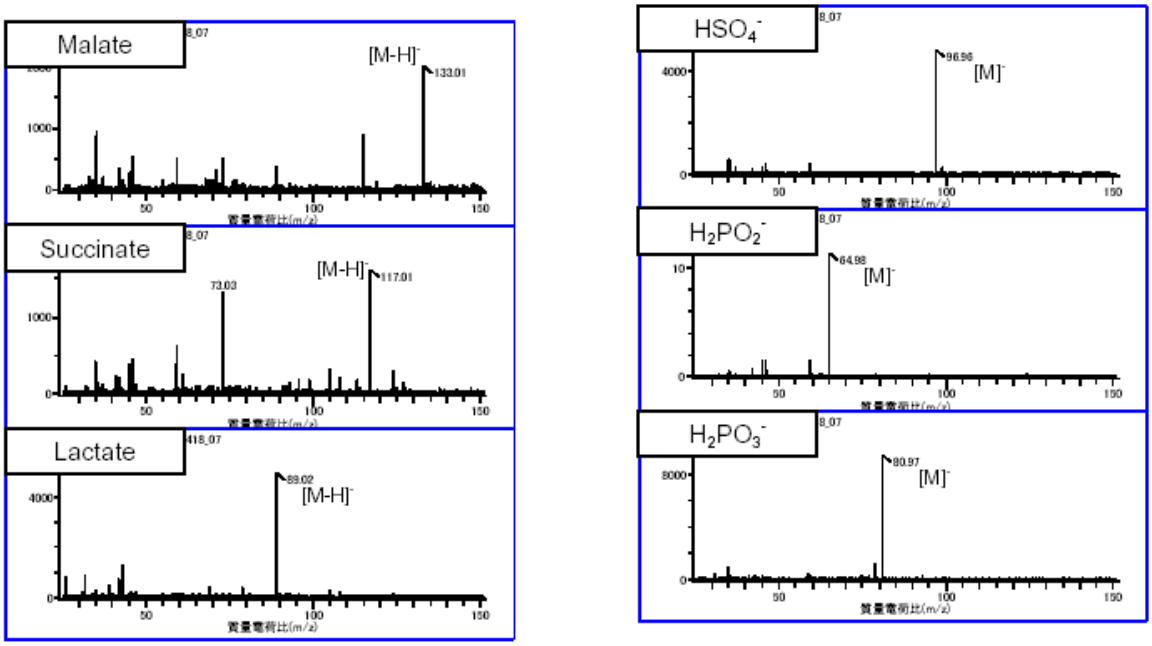


Figure 2. Mass spectra of anions in Sample (1)

Summary

In analyzing organic acids and inorganic anions in plating liquids, CE-MS detected low mass components at high sensitivity. Since successful separation of organic acids in LC requires highly concentrated inorganic buffers, .LC-MS is not appropriate for such application. CE-MS, requiring only a small volume of sample, was capable of analyzing plating liquids containing a great deal of inorganic components for a longer period of time with less contamination than LC-MS. Our experiment demonstrates that CE-MS is effective for analysis of organic acids in plating liquids.

MS Tips No.41 Analysis of Bromic Acids by Ion Chromatography (IC)/MS

Ion chromatography (IC) is designed to separate and analyze cations or anions using an ion exchange column. IC, typically integrating an electric conductivity detector, is used in a wide range of fields for quantitative analysis of ionic components. It is not suited for qualitative analysis because it uses the retention time alone when identifying components.

Mass spectrometry (MS) is combined with different types of chromatography as an optimum means for qualitative and quantitative analysis. Presently, MS is rarely combined with IC, because IC uses highly concentrated inorganic buffers as a mobile phase. Recently, however, most of the inorganic buffers can be diluted by a device, called the suppressor, to a negligible level immediately before being introduced to MS.

We have analyzed a bromic acid (BrO_3-) in the LC-TOFMS JMS-T100LC connected to Tosoh ion chromatograph IC-2001.

Experiment

Bromic acid is a type of halogen acid suspected of being carcinogenic. Bromic acid is found in bread as a residue from potassium bromite used as a dough enhancer. It is also used for ozone treatment in tap water. The revised 2004 Water Works Law stipulates the permissible level of bromic acid to be 0.01 mg/L with a fluctuation of 10% or less at 1/10 of the permissible level. This requires a technique designed to analyze 0.001 mg/L (1 ppb) solutions with high stability. The method officially selected by the government uses ion chromatography (IC)-post column (PC) (tribromide ion method), which has a quantitative limit of 1 ppb, not enough for accurate analysis. It also uses strong acid in post-column reaction, a problem in system operation and maintenance. Therefore, we have tested high sensitivity quantitative analysis using MS as a detector.

MS Conditions		IC conditions	
Unit	JMS-T100LC	Unit	IC-2001 (Tosoh)
Ionization mode	ESI-	Column	SHODEX SI-50 (ID 2 mm, 150 mm long)
Needle voltage	-1500 V	Guard column	TOSOH Super IC-AP (ID 2mm, 10 mm long)
Ion guide voltage	750 V	Mobile phase	5.0mM $NaHCO_3$
		Flow rate	0.3 mL/min
		Injection volume	50 µL

Conditions

Results

Figure 1 shows mass chromatograms of the standard bromic acid. The mass range was m/z128.934±0.05.The system detected up to 50 ppt with sufficient sensitivity. The standard curve had a good linearity from 100 ppt to 10 ppb (R^2 0.9998) as Figure 2 shows. RSD (n=7) of the peak area of the 1 ppb solution was 1.9%, demonstrating good reproducibility (Table 1).

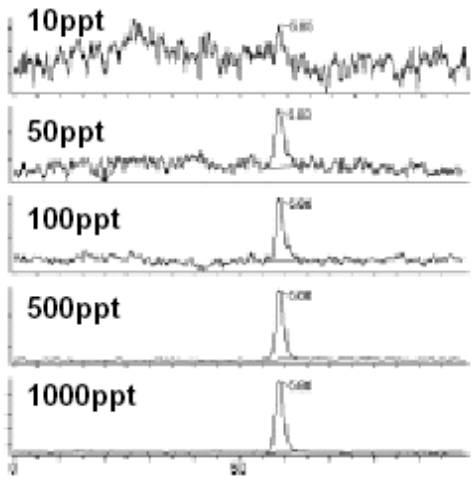


Figure 1. Mass chromatograms of BrO_3- (m/z 128.934±0.05)

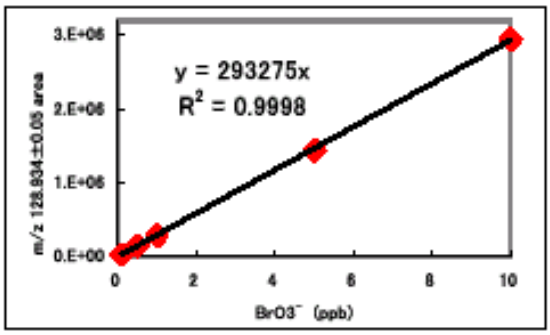


Figure 2. Detection curve of BrO_3- (100 ppt to 10 ppb)

n	m / z 128.934±0.05 1ppb
1	271328.83
2	273114.38
3	259482.15
4	265337.36
5	265793.56
6	265478.32
7	272979.19
Average	267645

Table 1 Reproducibility of peak area in 1 ppb BrO_3-

Figure 3a shows the mass chromatogram of tap water analyzed. The data shows high sensitivity quantitation at 0.41 ppb. Figure 3b is the mass chromatogram of tap water spiked with 1 ppb of bromic acid, demonstrating satisfactory results of a quantitative level of 1.37 ppb and a recovery of 96.6%.

Figure 4 shows mass chromatogram acquired from river water analyzed in the same manner. The quantitative levels were 0.11 ppb and 1.06 ppb (recovery 95.5%) respectively. The results demonstrate that the system analyzed environmental samples with no effect from impurities.

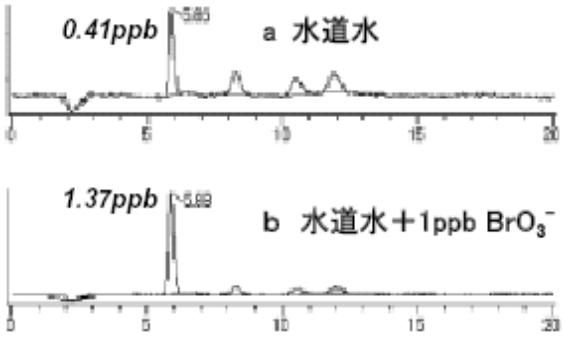


Figure 3 Analysis of bromic acid in tap water
a) Tap water only
b) Tap water + 1 ppb BrO_3-

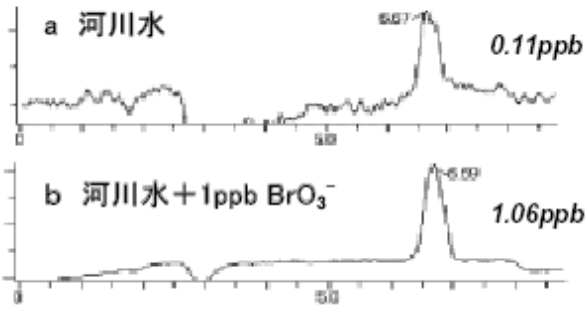


Figure 4 Analysis of bromic acid in river water
a) River water only
b) River water + 1 ppb BrO_3-

We also performed qualitative analysis of the river water with 0.11 ppb bromic acid. Figure 5 shows the mass spectrum of the target component in the river water. Table 2 shows measured and calculated values of m/z 129.The system analyzed the sample at a low concentration of 1 ppb with an error of 2 mmu or less. The system, capable of qualitative and quantitative analyses, produced successful attribution results of bromic acid, demonstrating its enhanced reliability.

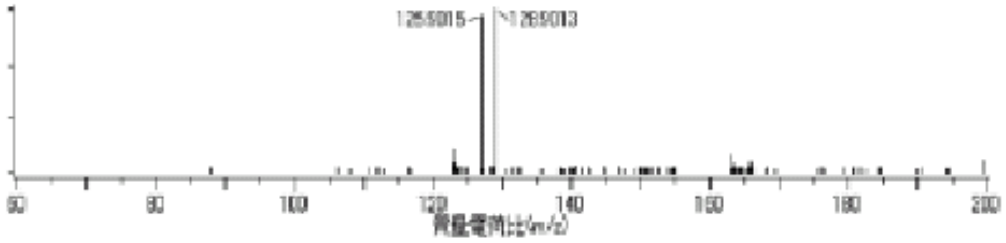


Figure 5 Mass spectrum of bromic acid in river water

	IC R.T.	Mesured MS	Formula ^{79}Br	^{81}Br	O	Calculated MS	Error (mmu)	(ppm)
River water (0.11ppb)	6.67'	126.90154	1	0	3	126.90308	-1.54	-12.13
		128.90129	0	1	3	128.90104	+0.25	+1.98

Table 2 Calculated results of m/z 127 and m/z 129 in river water

Summary

We were able to analyze bromic acid in IC/MS more efficiently and with higher sensitivity than in the method officially recommended by the government. Combining IC/MS with LC-TOFMS, we were also able to identify the components by exact-mass measurement, indicating that the system is applicable to qualitative analysis, which was not supported in IC alone. The results of our experiment show that IC/MS is an efficient and practical analytical technique. IC/MS is expected to have a wide range of applications in the future.

Acknowledgement

This paper is based on the lecture presented by Mr. Koki Shimizu, Synthetic Chemical Research Institute, Sankyo Chemical, and the accompanying literature distributed at the 2004 JEOL MS Users Meeting. We thank Mr. Shimizu for his permission to use his data.

MS Tips No.36 Cold-Spray TOFMS: Analysis of Porphyrin Isomers by AccuTOF CS

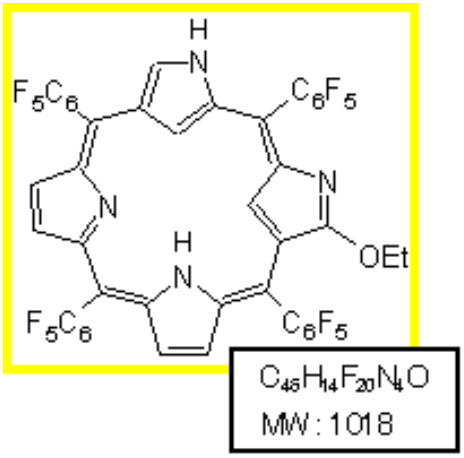
Dr. Furuta at Kyushu University has been studying membrane transport of proton and specific anions using porphyrin compounds. He has reported that multiple N-confused expanded porphyrin, which combines rotating and expanding characteristics of intramolecular pyrrole ring in N-confused porphyrin (NCP), an isomer of porphyrin, is effective for membrane transport.[1)-3)]

N-confused porphyrin is known to bond with a number of metal elements to form relatively stable complexes. An N-confused porphyrin metal complex has a carbon-metal bond within a ring, acting as an organic metal complex.

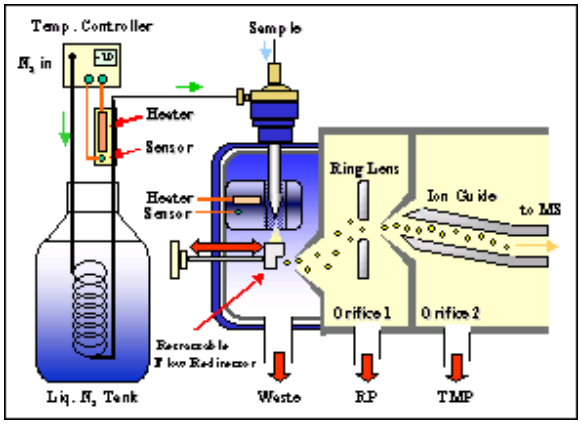
With confused pyrrole introduced into the ring, the complex will become unstable, and will be unfit for conventional ESI. Cold-spray ionization is more effective for such unstable samples. The figure below shows an outline of a cold-spray system.(For details of cold-spray ionization, see MS Tips No. 035.)

We used doubly N-confused porphyrin and its copper complex as samples to test the effectiveness of cold-spray ionization. We analyzed the samples in ESI and cold-spray, and compared the mass spectral data acquired under each set of conditions.

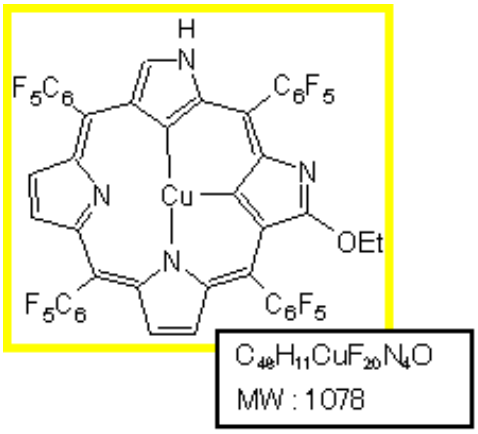
External view of AccuTOF CS



Doubly N-confused porphyrin (NCP)



Cold-spray system



Doubly N-confused porphyrin copper complex (NCP-Zn)

Results

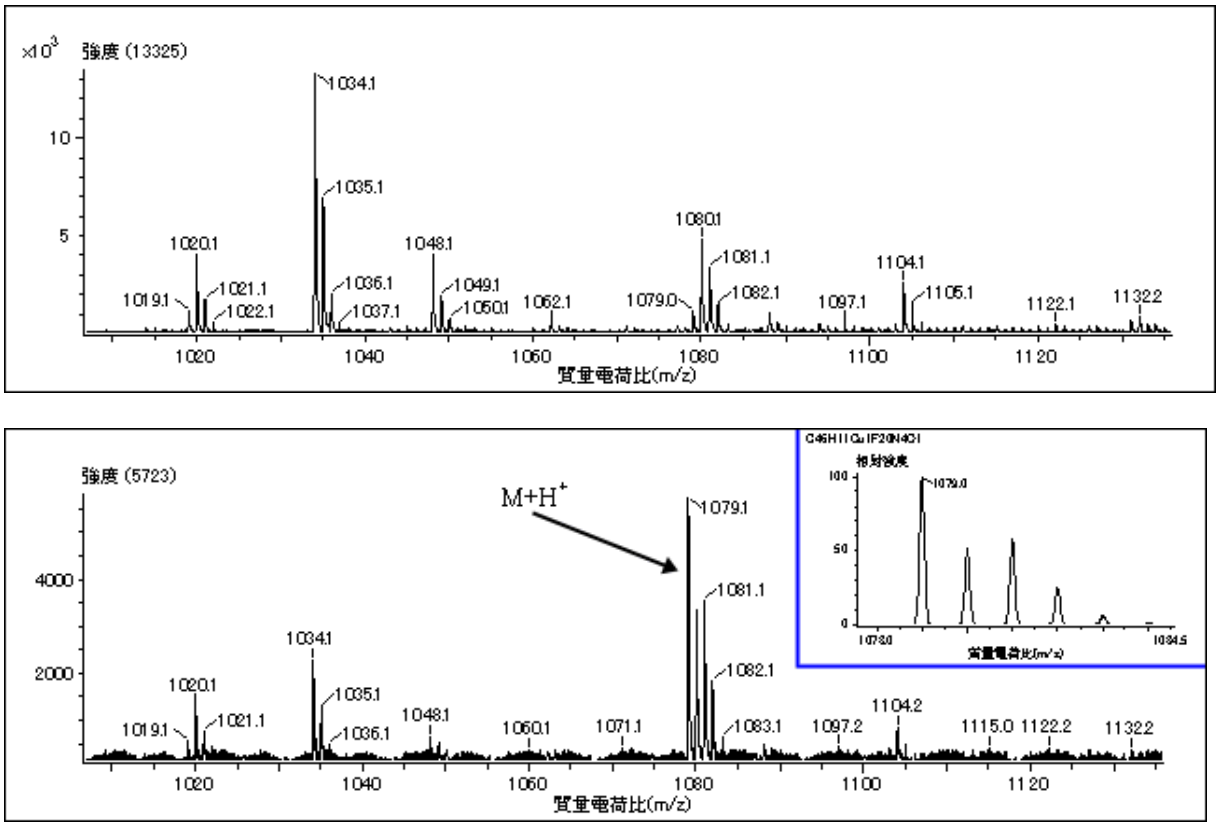
Both ESI and cold-spray detected the $M+H^+$ ion (m/z 1019) as the base peak of doubly N-confused porphyrin (MW: 1018).The spectral patterns acquired were nearly equal.

Only cold-spray detected the molecular ion of N-confused porphyrin copper complex. The isotopic simulation spectra showed an excellent agreement. While ESI detected an ion peak at the m/z nearby, the isotopic pattern of the spectrum acquired suggests that the composition contains no copper and is consequently an ion different from the target compound.

The results demonstrate that cold-spray will be a powerful tool in porphyrin chemistry, expected to have a wide range of applications including functional materials and reactive catalysts.

Conditions (N-confused porphyrin metal compound)	
Sample introduction	Infusion with syringe pump
Solvent	Chloroform
Flow rate	10 µl/min
Ionization	ESI and cold-spray
Coolant	Liquid nitrogen
Heater temperature	-10°C
Desolvating temperature control	250°C (ESI), OFF (cold-spray)
Orifice 1 temperature control	80°C (ESI), OFF (cold-spray)
Nebulizing gas	N_2 (1.0 L/min)
Drying gas	ON (ESI), OFF (cold-spray)

Needle voltage	2000 V
Ring lens voltage	15 V
Orifice 1 voltage	100 V
Orifice 2 voltage	5 V
Ion guide voltage	2500 V
Detector voltage	2800 V
Mass range	m/z 100 to 2000
Experiment time:	3min
Recording interval	5sec



Top: ESI mass spectrum of NCP-Zn

Bottom: Cold-spray mass spectrum and isotopic simulation mass spectrum of NCP-Zn

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