

Analysis of Contaminated Samples by DPiMS-2020 (1): Detection of Surfactants in Beverages

T. Murata, K. Waki

User Benefits

- ◆ Analysis by the PESI method is fast and simple, and does not require complex sample preparation.
- ◆ A technique that enables simple judgment of the presence of detergents (surfactants) in beverages was developed.
- ◆ Simple and high sensitivity screening for contamination by foreign substances is possible.

Introduction

A diverse range of cases of adulteration or contamination of beverages and food products by foreign substances has been reported, including contamination by familiar chemical substances. For this reason, an enormous number of chemical substances must be treated as analysis targets in inspections of beverages and food products when contamination is suspected. To conduct this kind analysis efficiently, it is necessary to develop a quick and accurate screening technique for the presence of contaminants.

In this research, a high sensitivity detection technique using the simplest possible sample preparation procedure was developed, assuming contamination of beverages by dishwashing detergents (surfactants), which is a frequent type of product contamination. This article also reports the results of a study of the applicability of this technique as a simple screening method for medicinal toxicants in beverages suspected of contamination.

Usefulness of PESI Method

In this experiment, the probe electro spray ionization (PESI) mass spectroscopy method was used as a fast and accurate screening method for the presence of contaminants. In this method, sampling is done by thrusting a probe into the sample, direct ionization of the components adhering to the probe, and analysis of the ionized sample in the MS section are conducted. Because this technique is highly resistant to the effects of the matrix during ionization, sample preparation such as extraction with an organic solvent is not necessary, and as a result, fast and simple analysis is possible. Based on this feature, PESI is expected to be extremely useful in cases involving contamination by foreign substances, in which a fast and comprehensive analysis of a large number of samples is necessary.

Sample Preparation and Analysis Conditions

As targets of analysis, seven commercially-available dishwashing detergents (A to G) were used. These detergents were diluted with one of four types of commercially-available beverages (barley tea, carbonated beverage, sports drink, milk tea) or distilled water and used as samples for study. The types of surfactants contained in the detergents were confirmed by a preliminary analysis following the procedure in a previous report⁽¹⁾. Samples for the analysis were prepared by adding equal quantities of 2-propanol to these contaminated beverages and mixing.

The DPiMS-2020 direct probe ionization mass spectrometer (Fig. 1) was used in the analysis. 9 µL of the sample solution was injected into a dedicated sample plate and analyzed. Tables 1 and 2 show the probe drive conditions and the analysis conditions of the mass spectrometer, respectively.

Table 1 PESI (Probe) Drive Conditions

Ionization position	: -37 mm
Ionization stop time	: 200 msec
Sampling position	: -46.3 mm
Sampling stop time	: 50 msec
Probe speed	: 250 mm/s
Probe acceleration	: 0.63 G



Fig. 1 Appearance of DPiMS™-2020

Table 2 Mass Spectrometer Analysis Conditions

DL temperature	: 250 °C
Heater block temperature	: 30 °C
Interface voltage	: ±2.45 kV
Scan speed	: 5000 µ/s
Data acquisition time	: 0 - 1 min: Negative mode 1 - 2 min: Positive mode

Table 3 List of Target Compounds of Analysis

Component	Surfactant	Target Compound	Detected ion
A	Alkyl sulfate (C13)		<i>m/z</i> 279 (-)
	Alkyl ether sulfate (C13)		<i>m/z</i> 323, 367, 411 (-)
	Alkylamine oxide (C12)		<i>m/z</i> 230, 459 (+)
B	Alkyl sulfate (C12)		<i>m/z</i> 265 (-)
	Alkyl ether sulfate (C12)		<i>m/z</i> 309, 353, 397 (-)
	Alkylamine oxide (C12)		<i>m/z</i> 230, 459 (+)
C	alpha-olefin sulfonate (C14)		<i>m/z</i> 275 (-)
	Alkyl ether sulfate (C13)		<i>m/z</i> 323, 367, 411 (-)
	Alkylamine oxide (C12)		<i>m/z</i> 230, 459 (+)
D	Alkyl sulfate (C12)		<i>m/z</i> 265 (-)
	Dialkyl sulfosuccinate (C8)		<i>m/z</i> 421 (-)
	Alkylamine oxide (C12)		<i>m/z</i> 230, 459 (+)
E	Dialkyl sulfosuccinate (C8)		<i>m/z</i> 421 (-)
F	Alkyl sulfate (C12)		<i>m/z</i> 265 (-)
	Dialkyl sulfosuccinate (C8)		<i>m/z</i> 421 (-)
G	Alkylamine oxide (C12)		<i>m/z</i> 230, 459 (+)

■ Analysis of Dishwashing Detergents

Dishwashing detergents are commercial products containing single or multiple types of surfactants. When the dilute aqueous solutions of the seven types of dishwashing detergents were analyzed, specific ions originating from surfactants were remarkably detected in all products. Table 3 shows the detected surfactant components and their specific ions. The same tendency as in these results was also confirmed in ionization by ESI.

Next, contaminated samples with contaminant mixing ratios of 0.001 to 0.1 % were prepared by mixing the dishwashing detergents with barley tea, carbonated beverage, milk tea, and a sports drink, and an analysis was carried out by PESI-MS. As in the above-mentioned measurements of the detergents, sample preparation was limited to addition of equal quantities of the organic solvent. For comparison, data were also collected from the uncontaminated beverages (blank beverages). The judgment criterion for detection of a foreign substance was detection in which the ratio of the detection intensity of the ion originating from the target substance in a contaminated sample and that of the contaminant ion in the blank sample was 3 (= SN ratio 3) or higher. Fig. 2 shows the mass spectra obtained by analysis of a sample prepared by mixing detergent A in a carbonated beverage at a concentration of 0.01 % and the blank sample (carbonated beverage without contaminant). Ions originating from the detergent (negative mode: m/z 279, 323, 367, positive mode: m/z 230, 459) were detected in the spectrum of the contaminated beverage, indicating that the beverage was contaminated with the foreign substance.

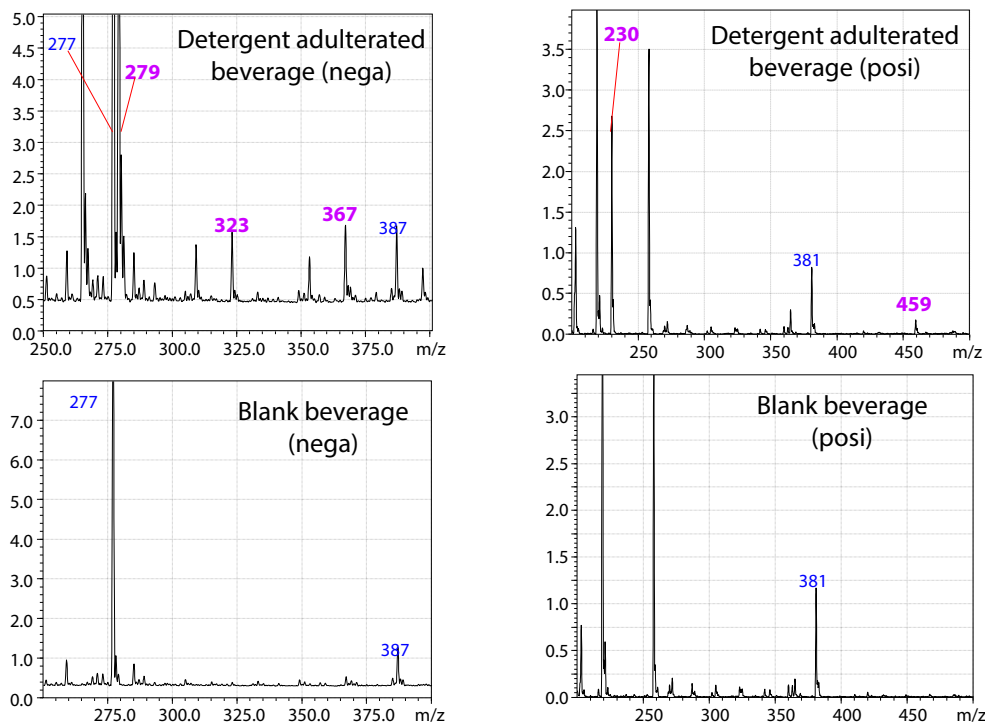


Fig. 2 MS Spectra of Carbonated Beverage Adulterated with Dishwashing Detergent A

Table 4 Detectable Concentrations of Beverages Adulterated with Dishwashing Detergents

Beverage	Concentrations of dishwashing detergents in beverages (%)						
	A	B	C	D	E	F	G
Distilled water	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Barley tea	<0.001	<0.001	<0.001	<0.001	0.005	<0.001	<0.001
Carbonated beverage	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Sports drink	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Milk tea	<0.001	<0.001	<0.001	<0.001	0.005	<0.001	<0.001

DPiMS is a trademark of Shimadzu Corporation in Japan and/or other countries.

Table 4 shows the results of an investigation of the limit of detection (LOD) by an analysis of the various detergent-contaminated beverages by the same method. In all the beverages, the surfactants in the beverages could be detected at product mixing rates of 0.005 % and higher (that is, when 50 μ L of the detergent was mixed in 1 L of the beverage), and it was possible to judge that the products were contaminated at this level of detection.

■ Conclusion

As the result of an analysis of samples contaminated with foreign substances (detergents) in the beverage by DPiMS-2020 direct probe ionization mass spectrometer, detection of surfactant components originating from the detergents was possible without special sample preparation. This result suggests that highly efficient screening for target substances in samples is possible by using the DPiMS-2020. Moreover, since it was also possible to detect contamination at levels on the order of 10 to 50 μ L/L, use as a screening method for contamination of liquids is expected in the future.

<References>

- (1) Nakano, S., Kamata, H., Sasaki, N., et al. J. Mass Spectrom. Soc. Jpn., 67(2), 53-63, 2019.
- (2) Misato Wada et al. Application of probe electrospray ionization mass spectrometry to the analysis of poisons and drugs in adulterated foods and beverages, Jpn. J. Forens. Sci. Technol.



Shimadzu Corporation
Analytical & Measuring Instruments Division
Global Application Development Center

www.shimadzu.com/an/

For Research Use Only. Not for use in diagnostic procedure.

This publication may contain references to products that are not available in your country. Please contact us to check the availability of these products in your country. The content of this publication shall not be reproduced, altered or sold for any commercial purpose without the written approval of Shimadzu. See <http://www.shimadzu.com/about/trademarks/index.html> for details.

Third party trademarks and trade names may be used in this publication to refer to either the entities or their products/services, whether or not they are used with trademark symbol "TM" or "®". The information contained herein is provided to you "as is" without warranty of any kind including without limitation warranties as to its accuracy or completeness. Shimadzu does not assume any responsibility or liability for any damage, whether direct or indirect, relating to the use of this publication. This publication is based upon the information available to Shimadzu on or before the date of publication, and subject to change without notice.

First Edition: Jan. 2021