

Contaminant Analysis by DPiMS™-2020 (2): Detection of Agricultural Chemicals in Beverages

T. Murata, K. Waki

User Benefits

- ◆ The PESI method enables quick and simple analysis without complex sample preparation.
- ◆ A simple technique for judgment of the presence of agricultural chemicals in beverages was developed.
- ◆ Simple and high sensitivity screening for the presence of contamination by foreign substances is possible.

■ Introduction

In incidents involving contamination or adulteration of beverages and foods, a diverse range of cases has been reported, including contamination by familiar chemical substances. For this reason, it is necessary to treat an extremely large number of chemical substances as analysis targets in inspections of beverages and foods in which contamination is suspected. To conduct this kind of analysis efficiently, it is necessary to develop a quick and accurate screening technique for the presence of contaminants.

In this article, a high sensitivity detection technique which requires only minimal sample preparation was developed using the DPiMS-2020 direct probe ionization mass spectrometer, assuming contamination of beverages by agriculture chemicals as an example of contamination. The results of a study of the possibility of applying this technique as a simple contamination screening method for beverages suspected of contamination are also reported.

■ Usefulness of PESI Method

In this experiment, an analysis was conducted using the probe electro spray ionization (PEI) method, in which sampling is carried out by thrusting a probe into the sample and directly ionizing the components adhering to the probe. Since quick and simple analysis is possible without extraction with an organic solvent or other complex sample preparation operations, PESI analysis is expected to be extremely useful in cases of contamination or adulteration, in which rapid and comprehensive analysis of a large number of samples is necessary.

■ Analysis of Agricultural Chemicals

The targets of this analysis were three types of glyphosate-based herbicides and one type of malathion-based insecticide, which are agricultural chemical preparations. These kinds of agricultural chemicals frequently contain various surfactants as additive ingredients to increase absorption of the active ingredient in the soil or plants. Therefore, these analyses were conducted focusing on both the active ingredient and the surfactant additive of the agricultural chemicals. The surfactant components contained in each of the agricultural chemicals were investigated and identified in advance by liquid chromatography mass spectrometry (LC/MS), as shown in Table 3.

First, the agricultural chemicals were analyzed by using the DPiMS-2020 direct probe ionization mass spectrometer. 9 μ L of the sample solution was injected onto a dedicated sample plate and measured under the probe drive conditions and mass spectrometry conditions shown in Tables 1 and 2, respectively.

In an analysis of dilute aqueous solutions of the three glyphosate preparations A, B, and C (preparations containing approximately 40% glyphosate), the detected ion peak at m/z 168 originating from deprotonated glyphosate was detected in the negative ion mode with all of the preparations (preparation content: 0.001 to 0.1%). A similar analysis of the malathion preparation D was also conducted, and ions originating from the proton adduct (m/z 331), the sodium adduct (m/z 353), and the potassium adduct (m/z 369) were detected in the positive ion mode (Table 3).

Table 1 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

Table 2 Mass Spectrometry 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 ion mode 1-2 min: Positive ion mode

Table 3 List of Target Compounds

Component	Agricultural chemical Target compound	Detection ion (positive (+) / negative (-))
H	Glyphosate	m/z 168 (-)
	Alkylbis (2-hydroxyethyl) Methylammonium (C10, 12, 14)	m/z 260, 288, 316 (+)
	Glyphosate	m/z 168 (-)
I	Polyoxyethylenealkylamine (C12, EO7 to 11)	m/z 494, 538, 582, 626, 670 (+)
	Glyphosate	m/z 168 (-)
J	Polyoxyethylene alkylphenylether (C9, EO8 to 11)	m/z 590, 634, 678, 722 (+)
	Alkylbenzenesulofonate (liner) (C12)	m/z 325 (-)
K	Malathion	m/z 331, 353, 369 (+)

Furthermore, in both the glyphosate preparations and the malathion preparation, ions originating from the surfactants used as additives were detected with remarkable intensity in the positive ion mode. Based on these results, the ions shown in Table 3 were used as monitor ions.

■ Analysis of Spiked Samples

Spiked samples were prepared by spiking barley tea, a carbonated drink, milk tea, and a sports drink with the above-mentioned agricultural chemicals (spike ratio: 0.001 to 0.1%), assuming cases of contamination of these commercially-available beverages with agricultural chemicals. The same sample preparation procedure as in the analysis of the agricultural chemicals was also used with these samples, and the analysis was carried out by the DPiMS-2020. As reference samples, data were collected for blank samples (beverage samples not spiked with the agricultural chemicals). The mass spectra obtained by this analysis were analyzed focusing on the ions originating from the components contained in the agricultural chemicals shown in Table 3. As the standard for judgment of contaminant detection, contamination was considered to be detected when the ratio of the detected intensity of the monitor ions in the spiked samples to the detected intensity of the impurity ions in the reference blank sample was 3 or larger.

Fig. 1 shows the result of an analysis of the milk tea spiked with agricultural chemical A (0.01% spike). Because ions originating from the agricultural chemical were detected, the sample can be regarded as contaminated with the chemical.

The beverages spiked with the other agricultural chemicals were measured in the same manner, and the limit of detection in each beverage was investigated. The results are summarized in Table 4. In the carbonated drink and the sports drink, glyphosate was detected at spike rates of 0.002% (equivalent to a product containing 20 µL of glyphosate per 1 L of beverage) or higher, and a judgment of contamination by the agriculture chemical was possible. In contrast, glyphosate could not be detected in the barley tea and milk tea at the spike rate of 0.01% (100 µL/L). However, a judgment of contamination was also possible in this case because various surfactants used as additives in the agricultural chemicals were detected. A similar analysis was carried out for the beverages spiked with the malathion preparation. Detection of malathion was possible at spike rates of 0.001% (10 µL/L) or higher in all the beverages except the milk tea.

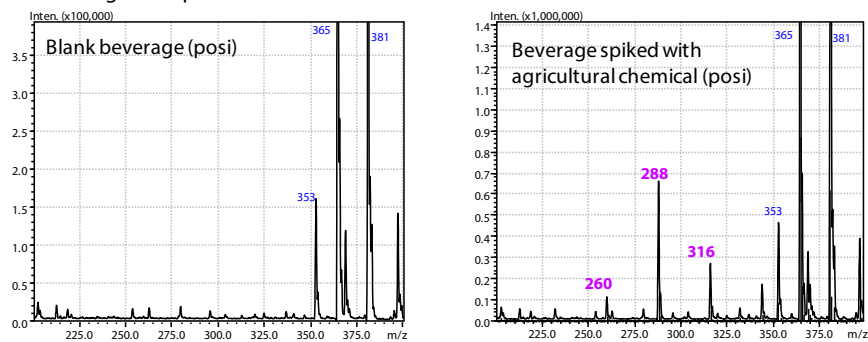


Fig. 1 MS Spectrum of Milk Tea Spiked with Agricultural Chemical A

Table 4 Detectable Concentrations of Agricultural Chemicals in Beverages

Beverage	Concentrations of agricultural chemicals in beverages (%)							
	Agricultural chemical A		Agricultural chemical B		Agricultural chemical C		Agricultural chemical D	
	Glyphosate	Surfactant	Glyphosate	Surfactant	Glyphosate	Surfactant	Malathion	Surfactant
Distilled water	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Barley tea	0.011	<0.001	0.02	0.008	0.02	0.01	<0.001	<0.001
Carbonated drink	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Sports drink	0.002	<0.001	0.002	<0.001	0.002	0.01	<0.001	<0.001
Milk tea	0.02	<0.001	0.03	0.01	0.03	0.01	> 0.1	0.02

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

On the other hand, in the milk tea, which has higher contents of proteins and fats than the other three beverages, malathion could not be detected even at the spike rate of 0.1% (1 mL/L). However, a judgment of the contamination of the milk tea was possible at spikes rates of 0.02% or higher because ions originating from the surfactants used as additives in the malathion preparation were detected in the negative ion mode.

These results revealed that a judgment of contamination is possible by this technique when beverages are contaminated with agricultural chemicals if the concentration of the agricultural chemical is 200 µL/L of beverage or more.

■ Conclusion

In this article, we attempted to use the PESI-MS method to determine whether beverages were contaminated with agricultural chemicals. Differences in the limit of detection of the active ingredients of the agricultural chemicals were recognized, depending on the type of beverage. However, even when the active ingredient of the agricultural chemical could not be detected, ions originating from surfactants used as additives could be detected with high sensitivity. Thus, this experiment demonstrated that it is possible to judge contamination by the PESI-MS method by an analysis targeting both the active ingredient and the ions originating from surfactant additives in agricultural chemicals at concentration levels as small as 200 µL/L of beverage or more. Based on this result, the technique described in this article is expected to be applied as a simple contaminant screening method.

<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: Apr. 2021