Application Note

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Rapid analysis of additives in food packaging

Using an Agilent 6120 Single Quadrupole MS System with an atmospheric pressure solid analysis probe (ASAP) and accurate mass identification by MassWorks

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Abstract

This Application Note describes the analysis of a compound extracted from food packaging using a direct probe ion source without chromatographic separation. The molecular formula for the detected compound was determined using Cerno MassWorks software. MassWorks uses an innovative calibration technology that increases the mass accuracy of single quad mass spectra. The presence of an additive in the food wrapper was determined by searching the molecular formula against a compound database.

Introduction

The applications of mass spectrometry (MS) have increased significantly over the last five years as systems have become easier and faster to use. However, sample preparation and liquid chromatography (LC) separation adds to the complexity and analysis time. Direct sample introduction into a mass spectrometer without separation by chromatography has recently received more attention.

One approach for direct ionization without chromatography is an atmospheric pressure solid analysis probe (ASAP) (Figure 1). ASAP is an effective tool to rapidly make a direct analysis of volatile or semivolatile substances in solid and liquid samples by atmospheric pressure ionization. This is a productive sample introduction approach when the sample is relatively simple, and does not require LC separation. In addition, the direct ionization of samples makes sample pretreatment or separation by chromatography unnecessary, thereby saving time.

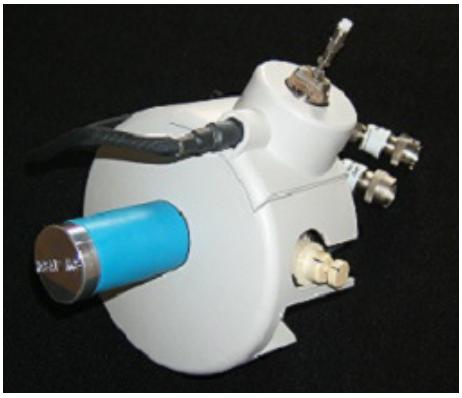

Figure 1. ASAP ionization source.

A single quadrupole mass spectrometer is powerful, inexpensive, and simple to operate, providing information related to the molecular weight of the target component. However, quadrupole mass spectrometry typically does not provide accurate mass data for identifying unknown compounds. To overcome this limitation, MassWorks was used to calibrate the MS data and transform them into accurate mass data. The calibration is accomplished by analysis of known calibration standards. The accurate mass data obtained from the quadrupole MS system could then be used to economically determine elemental compositions for unknowns found in a sample.

The ASAP was connected to the Agilent 6120 Single Quadrupole System to study the feasibility for rapid analysis of food packagings. To determine the elemental compositions of observed ions, the MS data were calibrated into accurate mass data through MassWorks, then analyzed with Calibrated Lineshape Isotope Profile Search (CLIPS).

Experimental conditions

Approximately 300 mg of a commercial food wrapper was weighed and dissolved in 5 mL of tetrahydrofuran (THF). The dissolved sample was applied to a glass capillary. To prevent overload, the excess sample was wiped away and the sample was introduced into the ionization source by inserting the capillary into the probe. The sample was vaporized by heated nitrogen gas in the ionization source, and ionized by corona discharge through atmospheric pressure chemical ionization (APCI). Figure 2 shows the complete sample introduction procedure.

Step 1: Apply a sample to the capillary.

Step 2: Insert the capillary into the probe, and insert the probe into the ionization source.

Step 3: Ionization starts.

Figure 2. Sample introduction procedure.

Figure 3 shows an infusion pump connected to the ASAP ionization source. For the calibration required by MassWorks and the subsequent elemental composition determination, a calibration standard was infused using the syringe pump. Vitamin D3 solution (100 ng/µL) was used as the standard, and introduced at a low flow rate (approximately 50 µL/min).

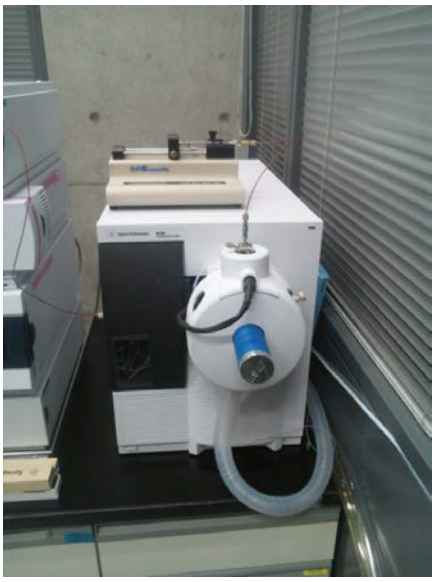

Figure 3. Overview of the ASAP/MS system with an infusion pump installed to introduce the calibrant used for accurate mass calibration by MassWorks.

Results and discussion

Figure 4A shows a total ion chromatogram obtained from an analysis of the THF extraction of a food wrapper. Figure 4B shows a mass spectrum after accurate mass calibration by MassWorks. After the introduction and data acquisition of the THF extracted food wrapper, the Vitamin D3 ($C_{27}H_{45}O^+$, *m/z* 385) standard solution was introduced from the infusion pump. A characteristic ion was found at *m/z* 403.2463 in the food wrapper sample by direct rapid analysis without chromatographic separation. A CLIPS search within MassWorks revealed the most likely elemental composition as $C_{20}H_{35}O_8^+$ (proton adduct) with the highest spectral accuracy of 99.5 %. Figure 5 shows the top six hits arranged in descending order of spectral accuracy, which measures the goodness of fit between the measured MS profile data after calibration and that calculated for the given formula candidate.

Note that the CLIPS formula search here was performed within the relatively larger mass error window of ±25 mDa, to account for the fact that only a single calibration ion was used for MassWorks calibration, as compared to multiple compounds across the mass range. Interestingly, only two possible elemental compositions are found with >99.0 % spectral accuracy, making it easy to rule out the distant 3rd and other candidates at <97.0 % spectral accuracy. This is a good illustration of the power of spectral accuracy in elemental composition determination.

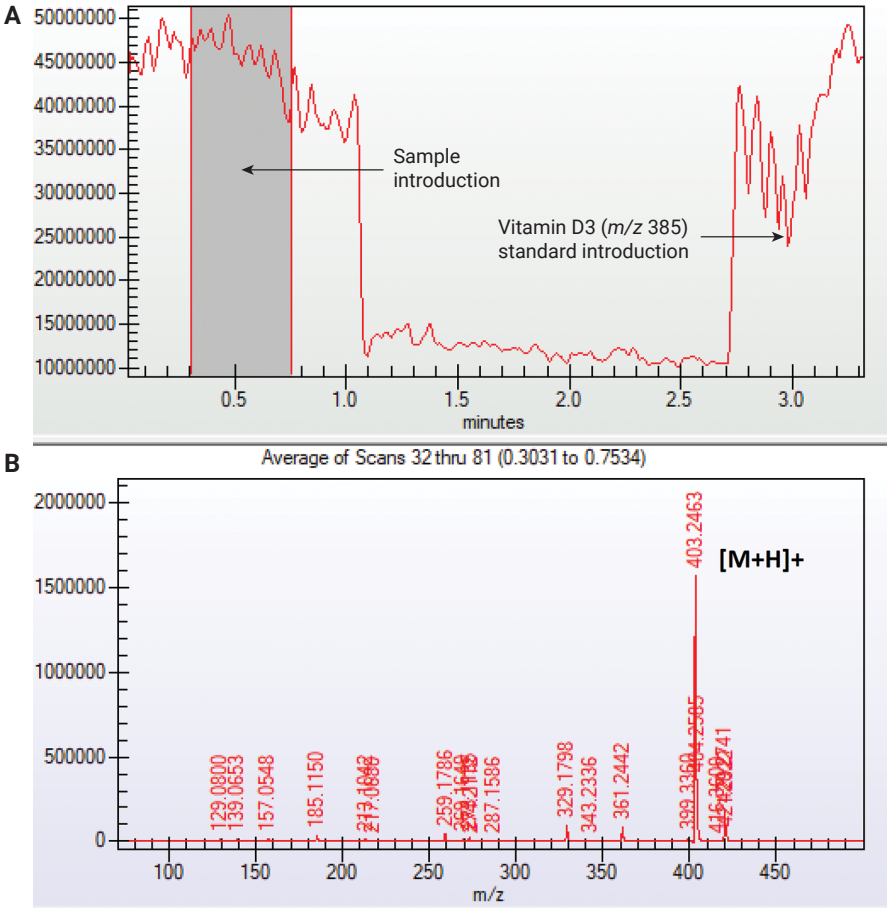

Figure 4. A) Total ion chromatogram for extract from a food wrapper introduced into the mass spectrometer using ASAP. B) Accurate mass spectrum resulting from MassWorks calibration for the analysis of extractables from a food wrapper.

CLIPS Results for average of scans 32 thru 81							
	Formula	Mono Isotope	Mass Error (mDa)	Mass Error (PPM)	Spectral Accuracy	RMSE	DBE
1	C20H35O8	403.2326	13.6555	33.8639	99.5178	2,819	3.5
2	C21H39O7	403.2690	-22.7300	-56.3676	99.2697	4,269	2.5
3	C24H35O5	403.2479	-1.6007	-3.9694	96.8556	18,381	7.5
4	C27H31O3	403.2268	19.5287	48.4288	94.3708	32,907	12.5
5	C28H35O2	403.2632	-16.8568	-41.8027	93.4936	38,034	11.5
6	C31H31	403.2420	4.2726	10.5955	91.0215	52,486	16.5

Figure 5. MassWorks CLIPS elemental composition determination results table for the unknown *m/z* 403.2463 ion.

This combination of the single quadrupole mass spectrometer with an ASAP installed and MassWorks software allowed rapid analysis and economical formula determination for unknown substances contained in a food wrapper.

Various public databases can be searched for the structure of the result obtained here. Figure 6 shows a hit from an online search in ChemSpider, one of the chemical databases, using the elemental composition obtained from this analysis. This hit points to acetyl tributyl citrate, a frequently used plasticizer in food wrappers.

Conclusions

We tested a rapid analysis approach for food wrappers using the Agilent 6120 Single Quadrupole Mass Spectrometer LC/MSD with an ASAP installed. This rapid analysis, including the calibration standard introduction required by MassWorks, was accomplished in minutes. With this calibration standard data from the rapid analysis, the MassWorks software can calibrate the quadrupole mass spectrometer data into accurate mass, allowing elemental composition determination of unknowns. With the obtained elemental composition, we searched a compound database and found an additive contained in a food wrapper. This study confirmed that this system configuration is applicable to the rapid and accurate mass analysis of additives.

The ASAP probe is an ionization source for direct analysis provided by IonSense, Inc.

MassWorks is a post processing MS calibration and analysis software provided by Cerno Bioscience.

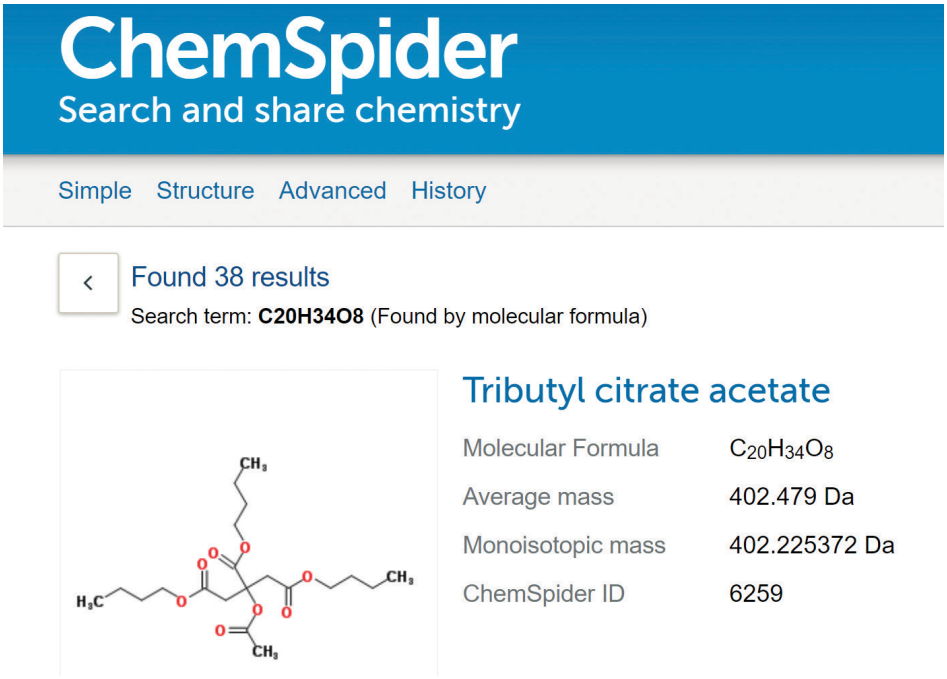

Figure 6. One example of ChemSpider search results for $C_{20}H_{34}O_8$.

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