

Screening for Phthalates Using the HM1000 Thermal-Desorption Mass Spectrometer

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1. Introduction

A revision to the European Union's *Restriction of Hazardous Substances (RoHS)*(2011/65/EU)—a set of EU directives regarding specific toxic substances—adds four species of phthalates^(*1) to the list of controlled substances as of July 2019. Phthalates are used as plasticizers added to substances such as resins and rubbers to increase flexibility. They are used particularly frequently in chloroethylene products such as sheaths for electrical wires, electrically insulating tapes, and packaging films, but are also used as materials for many other products—from toys, to appliances, to electronics, and indeed almost every imaginable type of consumer product.

The revised RoHS Directive states that, as of July 2019, any general-purpose electric or electronic device that includes quantities of controlled substances in excess of certain fixed thresholds may no longer be sold in the European marketplace; similar restrictions on medical devices go into effect in July 2021. This has created a need for many corporations to assess the content of phthalates in products and components and to develop strategies for controlling them.

A widely used technique for controlling environmentally restricted substances involves first conducting screening tests to identify cases in which quantities of controlled substances exceed or approach regulatory thresholds, then subjecting any such cases to more detailed analysis. X-ray fluorescence analyzers have been widely adopted as instruments for screening tests of RoHS Directive-regulated substances such as cadmium (Cd) and lead (Pb), and Hitachi High-Tech Science Corporation has a track record of developing and selling dedicated instruments intended exclusively for use in controlling environmentally restricted substances.

However, measurements of phthalates require component extraction via organic solvents and other steps that, if performed via conventional general-purpose screening techniques, are problematic in several ways: the procedure is time-consuming and involves complex instruments that employ large quantities of solvents, requiring expert-level knowledge and experience to operate. To address this situation, we have developed the HM1000 thermal-desorption mass spectrometer with the aim of enabling *rapid and simple measurements* of phthalates. In this report, we introduce this new instrument.

(* 1) The four types of phthalates affected are diethylhexyl phthalate (DEHP), benzyl butyl phthalate (BBP), dibutyl phthalate (DBP), and diisobutyl phthalate (DIBP). The maximum acceptable concentration is 0.1 wt% (1000 ppm).

2. Principles of Measurement

Figure 1 shows an external view of the HM1000 and an overview of its principles of measurement. The instrument consists of (a) a sample heating unit that vaporizes phthalates within a sample, (b) an ionizing unit that ionizes the vaporized phthalates, and (c) a mass spectrometer that analyzes the ionized components. In addition, the instrument is equipped with an autosampler to allow continuous automated measurement of up to 50 samples.

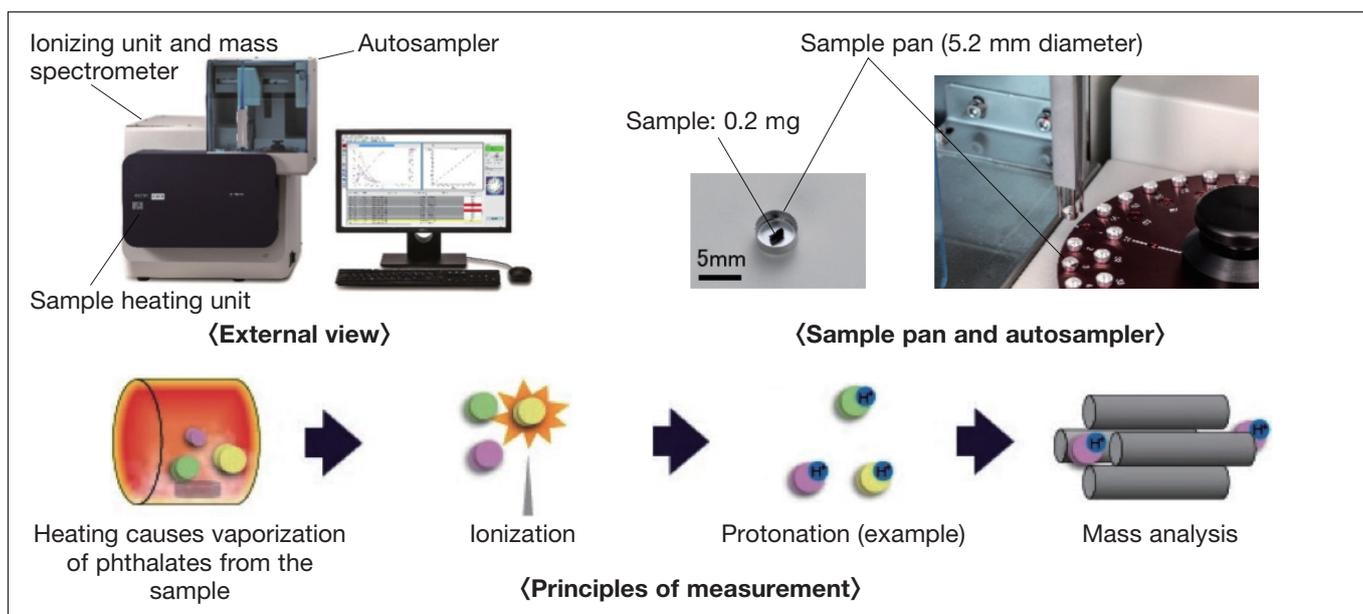


Fig. 1 External view of the HM1000 and its principles of measurement

An appropriate sliver (on the order of 0.2 mg) is cut from the sample and placed in a customized sample pan. Upon initiating the measurement, the autosampler transfers each sample pan, one at a time, to the sample heating unit, within which phthalates in vaporized form are released from the heated sample. The vaporized phthalates are ionized by the ionizing unit and subjected to mass analysis in the mass spectrometer. The ionization method used is atmospheric-pressure chemical ionization (APCI), in which the corona discharge created by applying a voltage to a discharge needle yields ionization via protonation. An advantage of the APCI method is that it rarely induces fragmentation (breaking of intramolecular bonds). This ensures that molecular structures are not destroyed by the ionization process, allowing direct analysis via mass spectrometer.

Figure 2 shows examples of mass spectra obtained by the HM1000 for the phthalates DBP, BBP, and DEHP1000 ppm. As indicated in the figure, upon protonation the three species are detected at mass/charge ratios of $m/z=279$ ion (DBP), 313 ion (BBP), and 391 ion (DEHP).

The time required to measure a single sample is approximately 10 minutes; by using the autosampler, one can make continuous automated measurements of 50 samples (including reference material) in approximately 8 hours. The entire process—from sample transport to measurement, quantification, and identification—is automated by specialized software, with no need for users to input conditions for the analysis. Users can initiate continuous automated measurements simply by specifying predetermined measurement recipes, and can thus easily assess the presence or absence of phthalates with no need for specialized knowledge or training.

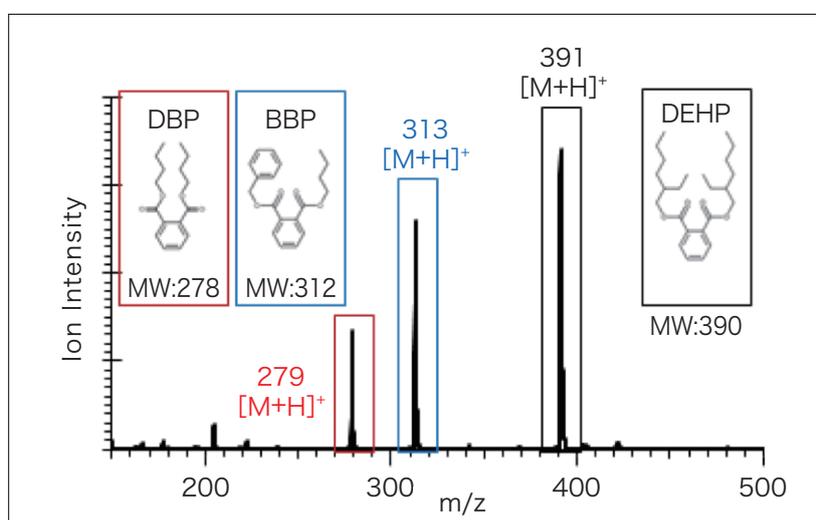


Fig. 2 Examples of mass spectra for phthalates

3. Measurement Case Studies

Two aspects of instrument performance that are important for applications to screening tests are:

- (1) *Measurement time*: Testing large numbers of samples in the shortest possible time.
- (2) *Detection sensitivity*: Achieving high-precision measurements to reduce indeterminate measurements—that is, cases in which a measurement fails to determine whether or not a sample contains unacceptable levels of phthalates, in which case more precise analysis is needed.

In this section, we present practical examples that demonstrate that the high performance of the HM1000 is more than adequate to meet these needs.

3-1. Measurement time

An important goal in screening testing is to reduce the amount of time needed to test a single specimen, ensuring that many samples can be tested in a short amount of time. The HM1000 addresses this need by achieving rapid throughput: the phthalate content of a single test specimen can be measured in less than 10 minutes.

To achieve reduced measurement times, it is necessary to reduce the amount of time required to heat the sample until its phthalate content has been fully vaporized. Indeed, we cannot achieve correct measurement results if we do not detect the full volume of phthalate contained in a sample. The HM1000 incorporates a newly designed sample heating unit—capable of rapidly increasing sample temperature—that allows essentially all phthalates contained in a solid sample to be almost fully vaporized upon heating for just 7 minutes.

Figure 3 plots the results of an HM1000 measurement of the certified reference material NMIJ CRM 8152-a. The horizontal axis indicates the time elapsed since the start of the measurement, while the vertical axis indicates the ion intensities of the various phthalates. As these results demonstrate, within 7 minutes of the start of measurement the ion intensity has died down substantially—even for DEHP, the most difficult to vaporize of all the phthalates regulated by RoHS Directive. This confirms that the HM1000 can fully vaporize the entire phthalate content of a sample in just 7 minutes of measurement time.

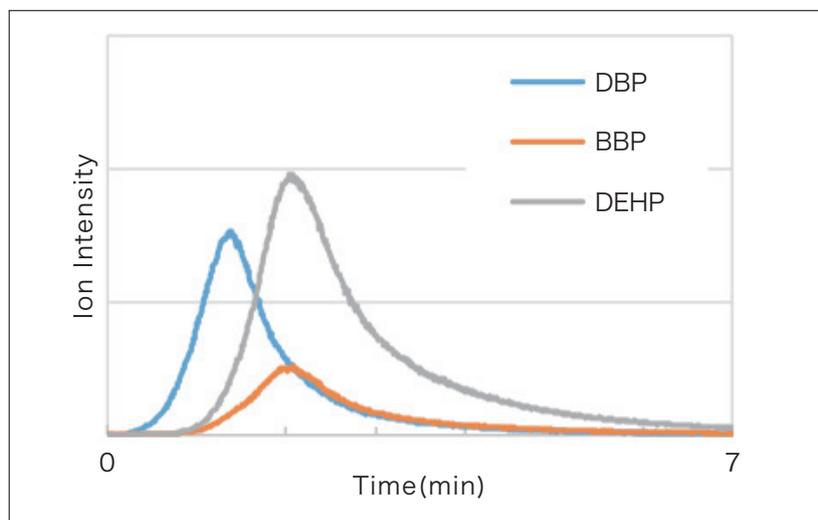


Fig. 3 Ion intensity profile for NMIJ CRM 8152-a

3-2. Detection thresholds

Although increased throughput is an important necessity for screening tests, the *accuracy* of measured results is an even more crucial requirement. Indeed, no matter how quickly an instrument might make a measurement, if the instrument's detection capabilities are inadequate then it will inevitably produce indeterminate results for many samples. In such cases, the instrument user must re-analyze the indeterminate sample using more precise analysis to establish definite conclusions. Thus, if a large proportion of samples produces only indeterminate results, the time and cost required to yield conclusive information will only grow, calling into question the entire purpose of the screening protocol.

The HM1000 eliminates such concerns by achieving a lower-limit detection threshold for phthalates of just 100 mg/kg or lower—to be compared to the RoHS Directive threshold of *1,000 mg/kg*—thus more than comfortably satisfying the accuracy requirements demanded of instruments for screening tests.

Figure 4 shows ion-intensity profiles for samples containing various concentrations of phthalates. The measurement samples were prepared by dripping 500 mg/kg, 100 mg/kg, or 0 mg/kg (blank sample) of a standard solution containing a mixture of phthalates into a polyvinyl chloride (PVC) solution, and then extracting the solvent at room temperature and drying. The horizontal plot axis indicates time since the start of measurement, while the vertical axis indicates ion intensities of the various phthalates. As is clear from this figure, a concentration of just 100 mg/kg of any phthalates suffices to ensure a clearly identifiable peak.

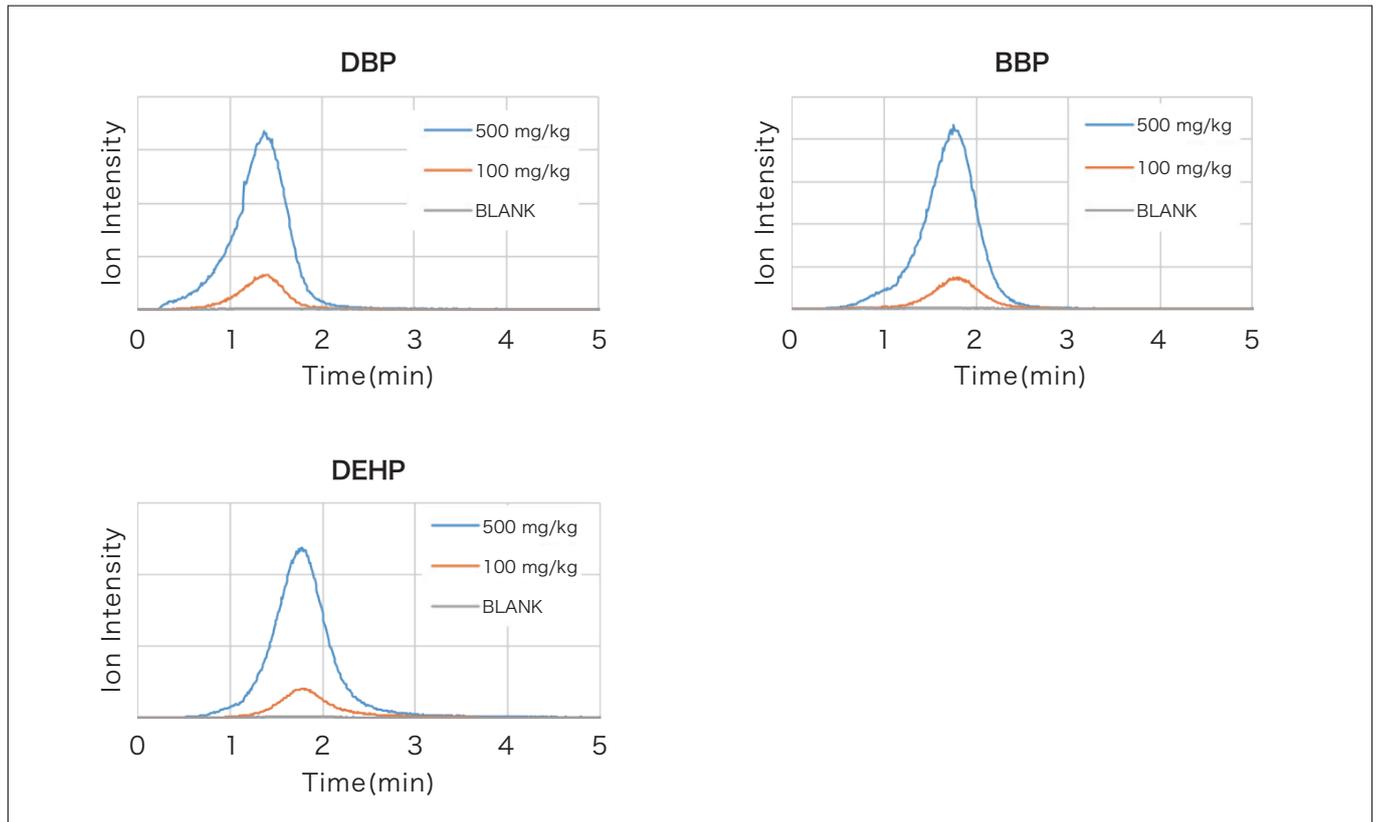


Fig. 4 Ion intensity profiles for phthalates at various concentrations

4. Conclusions

In this report, we introduced the HM1000, a thermal-desorption mass spectrometer that enables rapid and simple measurements of phthalates, substances that have recently become a prominent focus of attention due to revised RoHS Directive restricting their use. We described the configuration of the HM1000, discussed the principles underlying its measurements, and presented a number of illustrative measurement applications. The HM1000 greatly simplifies the measurement process and allows even operators with no specialized knowledge or training to make high-quality measurements with ease. Moreover, the rapid throughput achieved by the instrument—with measurements of individual samples requiring just 10 minutes or less—makes it a promising tool for product or component manufacturers seeking to reduce costs and improve the efficiency of the phthalates screening process.

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