Construction of Phthalate Screening System

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1. Introduction

An official communication dated June 4, 2015 announced that the EU RoHS directive will ban the use of 4 types of phthalates as of July 22, 2019 (Table 1). In anticipation of these and other new additions to the list of regulated substances, BROTHER INDUSTRIES LTD. (hereafter simply "BROTHER INDUSTRIES") has been working since 2013 to investigate methods for eliminating such substances.

In this report, we discuss our collaboration with Hitachi High-Tech Science Corporation (hereafter simply "Hitachi High-Tech Science") to address the challenge of developing screening systems, focusing on the evolution of the new screening instrument we have developed and the substance-elimination method it enables.

Table 1: Overview of the new regulations

Substance	Abbreviation	CAS Number
Bis (2-ethylhexyl) phthalate	DEHP	117-81-7
Butyl benzyl phthalate	BBP	85-68-7
Dibutyl phthalate	DBP	84-74-2
Diisobutyl phthalate	DIBP	84-69-5

Effective July 22, 2019, the presence of the 4 types of phthalates listed above in electrical and electronic devices sold in the EU will be restricted to a maximum acceptable concentration of 0.1% (1,000 ppm), uniformly distributed throughout the material in question.
Note: For products in categories 8 and 9 (including in vitro diagnostic medical devices and industrial monitoring and control instruments), the restrictions will go into effect on July 22, 2021.

2. The State of the European Market[1)]

Plasticizers—additives used to improve flexibility and workability—contain phthalates. At present, plasticizers continue to be used in extremely high quantities.

In the EU, examples of violations related to chemical substances are noted and recorded, with over 400 cases identified in 2016 alone (Table 2). An analysis of the 2016 data reveals particularly large numbers of violations in two product categories: *toys* and *clothing*, *textiles*, *and fashion items* (Figure 1). In the category of *electronic devices*, one finds just 10 cases of violations, a relatively small number. Further subdividing violation instances by legislative category, and by the substance and the event responsible for the violation, reveals that cases constituting violations of REACH regulations are recorded with particularly high frequency for phthalates, which are present in the overwhelming majority of toys (Figures 2, 3). For this reason, although violations of the RoHS directive are currently decreasing, there are concerns that numbers of violations could once again spike—including in the category of *electronic devices*—after restrictions on the 4 new phthalates go into effect in July 2019.

Table 2: Numbers of violations of regulations regarding chemical substances or environmental protection, as recorded by the EU Rapid Alert System(＊1)

Year	Chemical substance / environmental protection(＊2)		TOTAL
	Number of violations	Fraction (%)	Number of violations
2005	83	11.6	713
2006	137	15.0	915
2007	281	21.1	1,332
2008	339	22.0	1,542
2009	490	29.4	1,668
2010	437	22.2	1,972
2011	337	21.9	1,542
2012	412	21.4	1,923
2013	494	24.4	2,026
2014	632	28.1	2,248
2015	551	29.7	1,855
2016	467	24.7	1,887
TOTAL	4,660	23.7	19,622

(＊1) Rapid Alert System: A system designed to protect the health and safety of consumers by facilitating rapid information exchange among EU government agencies and member nations.
(＊2) Includes RoHS, REACH, and CLP regulations

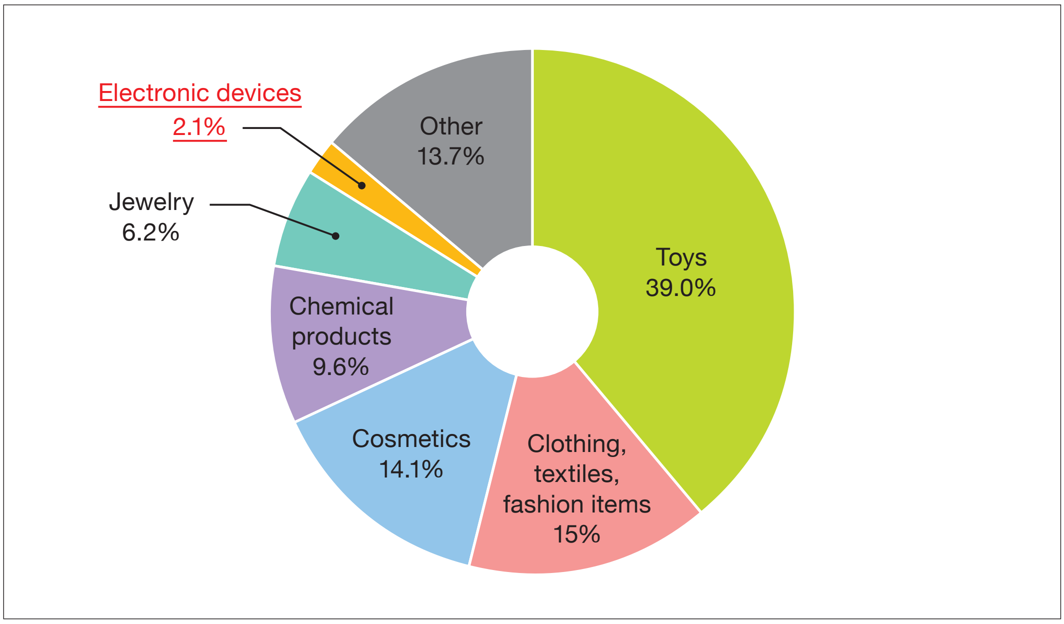

Fig. 1 Instances of regulatory violations, subdivided by product category

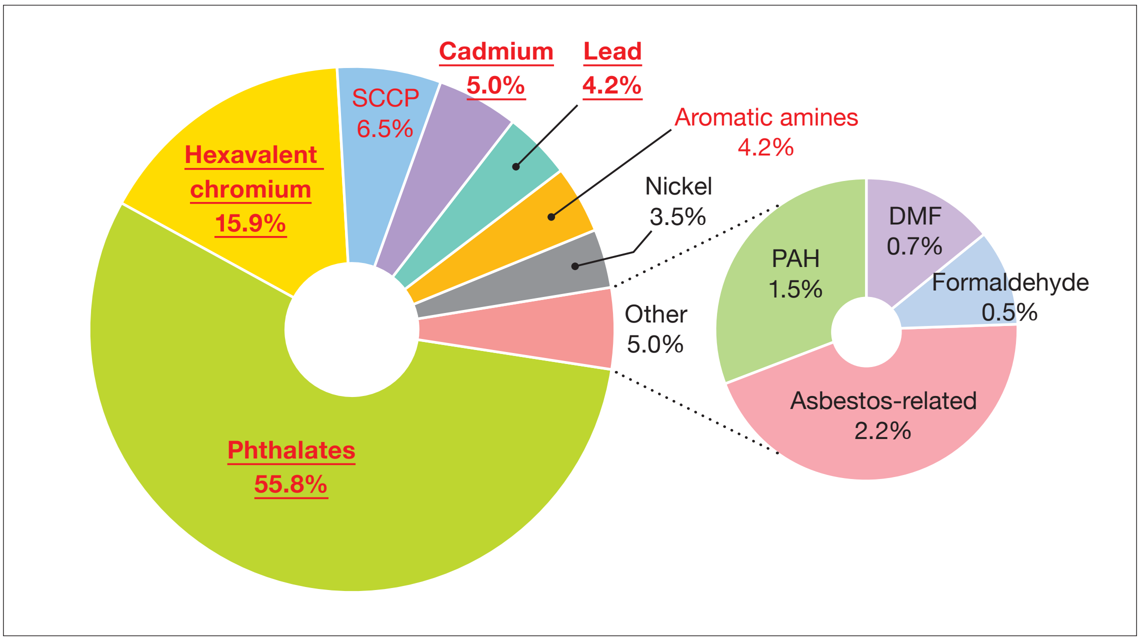

Fig. 2 Instances of regulatory violations, subdivided by offending substance and event. (Some violations are counted multiple times; we have extracted a representative sample.)

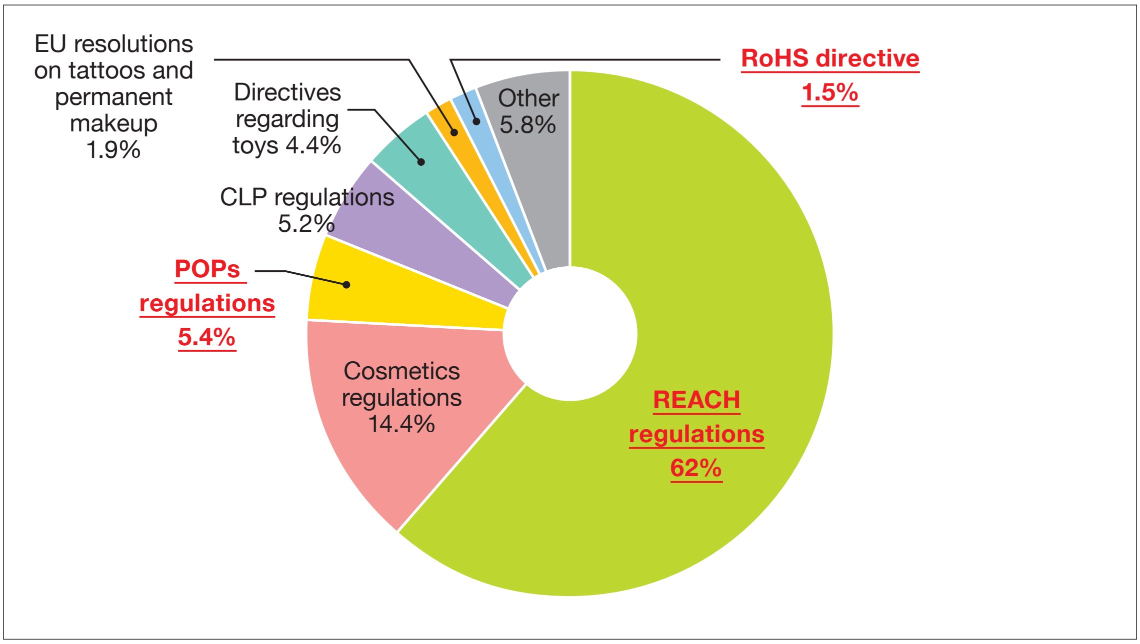

Fig. 3 Instances of regulatory violations, subdivided by legislative framework. (Some violations are counted multiple times; we have extracted a partial representative sample.)

3. Where Are Phthalates Hiding?[1, 2]

Phthalates are contained in a wide variety of products and are used as plasticizers, whereupon they are commonly found in products for which increased flexibility and workability are desirable. In particular, phthalates are frequently used to soften PVC (chloroethylene), and thus are commonly found in products such as PVC hoses and PVC coatings for cables for electrical and electronic products. Indeed, the phthalate DEHP—an SVHC[*2] that is already on the list of candidate substances for authorization[2] under the EU's REACH[*1] regulatory framework[3]—is imported as an article at quantities exceeding 1 ton per year and is found in an extremely wide variety of products, as is evident from the following list delivered to the ECHA[*3] and made available to the public (Table 3).

(＊1) Abbreviation for Registration, Evaluation, Authorization, and Restriction of Chemicals (underlined portion)
(＊2) Abbreviation for Substances of Very High Concern (underlined portion)
(＊3) Abbreviation for European Chemicals Agency (underlined portion)

Table 3: Examples of products suspected to contain the phthalate DEHP

Category	Products
Everyday products	Tablecloths, notebooks, pencil/pen cases, clocks, shoes, rain boots, sewing machines, wallets, umbrellas, raincoats, toolboxes, air mattresses, pillows, bathtubs, shower curtains, bath mats, wash tubs, shower caps, clothes hangers, document folders, doormats, anti-insect nets, gardening supplies, chairs, backpacks, bracelets, necklaces, pumps, suitcases, artificial leathers, fingernail polish, coin purses, furniture, washing machines, vacuum cleaners, massagers, training devices, hair dryers
Construction materials	Flooring materials, floor tiles, cords, fences, lamps, cushioning materials, covers, streetlights, overhead lights, floor coverings
Recreational equipment	Pavilions, tents, tarpaulins (autotype: sunshades used in auto camps), diving flippers, diving masks, boats, torches
Electrical and electronic products	Insulating materials, power cords, cables, wiring, electric wires, adapters, connectors, video, audio equipment, personal computers, keyboards, headphones, speakers, hubs, tripods, scanners, fax machines, webcams, air conditioners, shavers, air purifiers
Textiles and Fabrics	Buttons, zippers, labels, sequins (shiny accessories incorporated into stage costumes, often by female performers; also known as *paillettes*), decorative accessories, pajamas, printed fabrics
Vehicular	Wire harnesses, protectors, cables, cylinders, keys, motors, motorcycles, heater sensors, hoses, plugs, transmissions, caps, bearings, ventilation hoses, gaskets, cover holes, ashtrays, smoking accessories, passenger lifts, wind-blocking glass stoppers, noise suppressors, vehicle floor mats, speakers, rubber parts
Medical equipment	Artificial respirators, blood bags, platelet bags, dialysis machines, artery tubes, vein tubes, blood transfusion tubes, optical films, diagnostic equipment
Other	Polishing pads, goggles, protective gear, protective eyewear, bulbs, PVC products for reinforcing rubber (metal), adhesives (labels, films)

4. Development of a New Screening Instrument

Because the EU RoHS directive will soon prohibit the use of the 4 types of phthalates discussed above, manufacturers of electrical and electronic products must identify components containing high concentrations of these substances and reduce their content to within regulatory limits before the new regulations take effect. As noted in the previous section, phthalates are used in a wide variety of products. For this reason, conventional analysis methods typically proceeded by capturing phthalates in organic solvents, then using a gas chromatography mass analyzer to separate and measure the quantity of the offending substance. In the past few years an alternative method—in which a resin or similar sample is heated directly to vaporize the ingredients to be analyzed, and the vaporized gas is analyzed directly by a gas chromatograph mass analyzer—has also come into use. Although this method reduces the time required for the analysis and streamlines the operational burden, it requires supervisors and operators with expert knowledge of chemical analysis methods; moreover, because the method uses helium gas, it requires the installation of supply pipes or gas canisters.

At BROTHER INDUSTRIES, we have investigated a variety of methods for conducting screening at manufacturing sites to prevent phthalates from contaminating products. In conjunction with this effort, Hitachi High-Tech Science has developed screening instruments intended for use at manufacturing sites (Figures 4, 5).

Key Features:

- No preprocessing required: simply cut a specimen fragment of mass on the order of 0.2 mg and mount it in the instrument
- High throughput: measuring a single sample requires less than 10 minutes
- Reduced operational burden: autosampler allows simultaneous measurement of 50 test specimens
- Low maintenance costs: no need for helium gas or gas-chromatograph columns

Overview:

To use the instrument, one cuts a sample of a certain mass from the test specimen, mounts it in a sample vessel, and heats in a furnace to vaporize phthalates. The vaporized phthalates are ionized as-is and subjected to mass analysis.

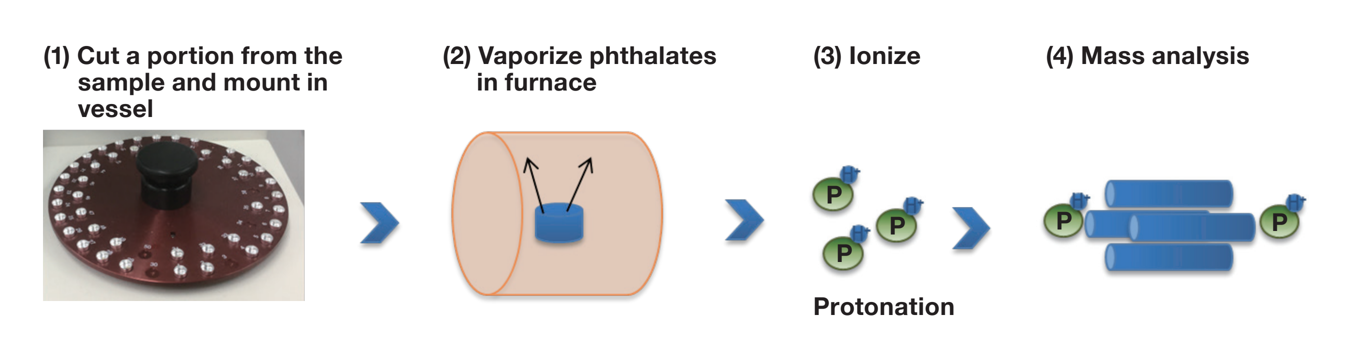

Fig. 4 Screening instruments and schematic illustration of measurement procedure

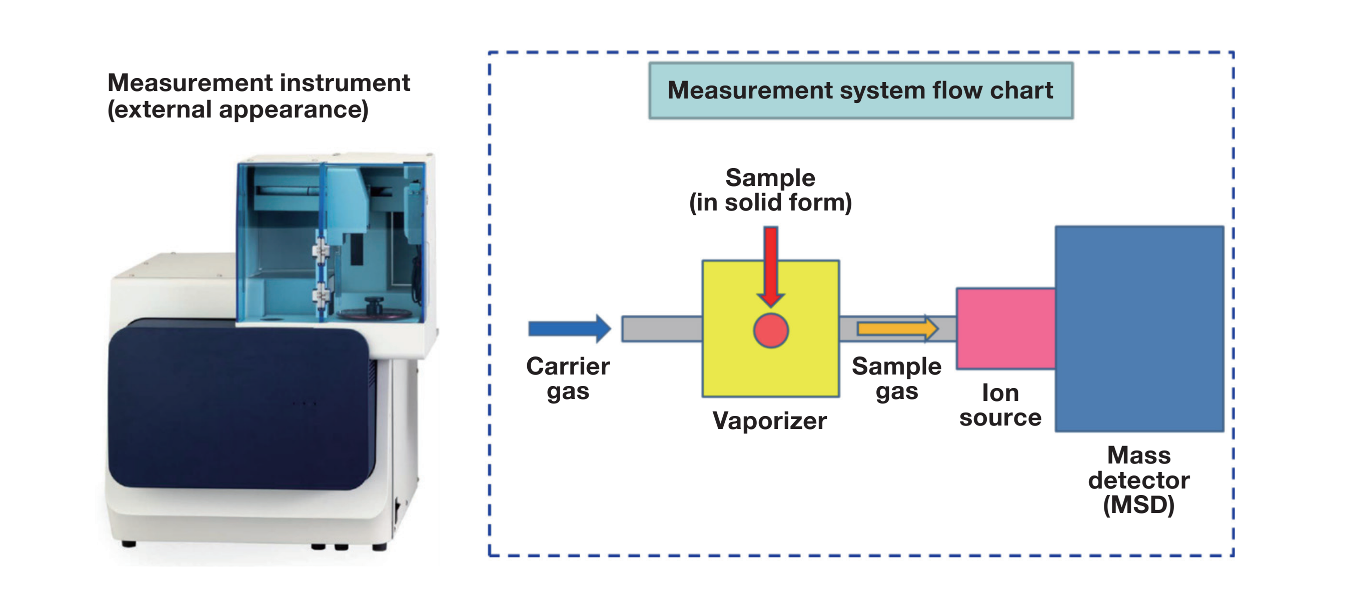

Fig. 5 The measurement instrument (external appearance and a flow chart of the measurement system)

The sample measurement discussed below (see Figure 6) demonstrates that, among the four types of phthalates discussed above, the system is capable of measuring quantities of DBP, BBP, and DEHP in short periods of time with extremely high sensitivity.

One characteristic of this system is that it cannot separately measure quantities of DBP and DIBP, as these molecules have identical masses.

However, this should not be problematic for the purposes of testing manufactured products for the content of regulated substances; indeed, both DBP and DIBP are subject to regulatory restrictions, and thus it suffices to measure the total quantity of both substances without distinguishing one from the other.

Although the system cannot separate molecules of identical masses, it has the advantages of offering short measurement times and requiring no helium gas (canisters), chromatograph columns, or gas supply pipes, allowing it to be installed anywhere. This newly developed screening instrument is extremely valuable for use in manufacturing.

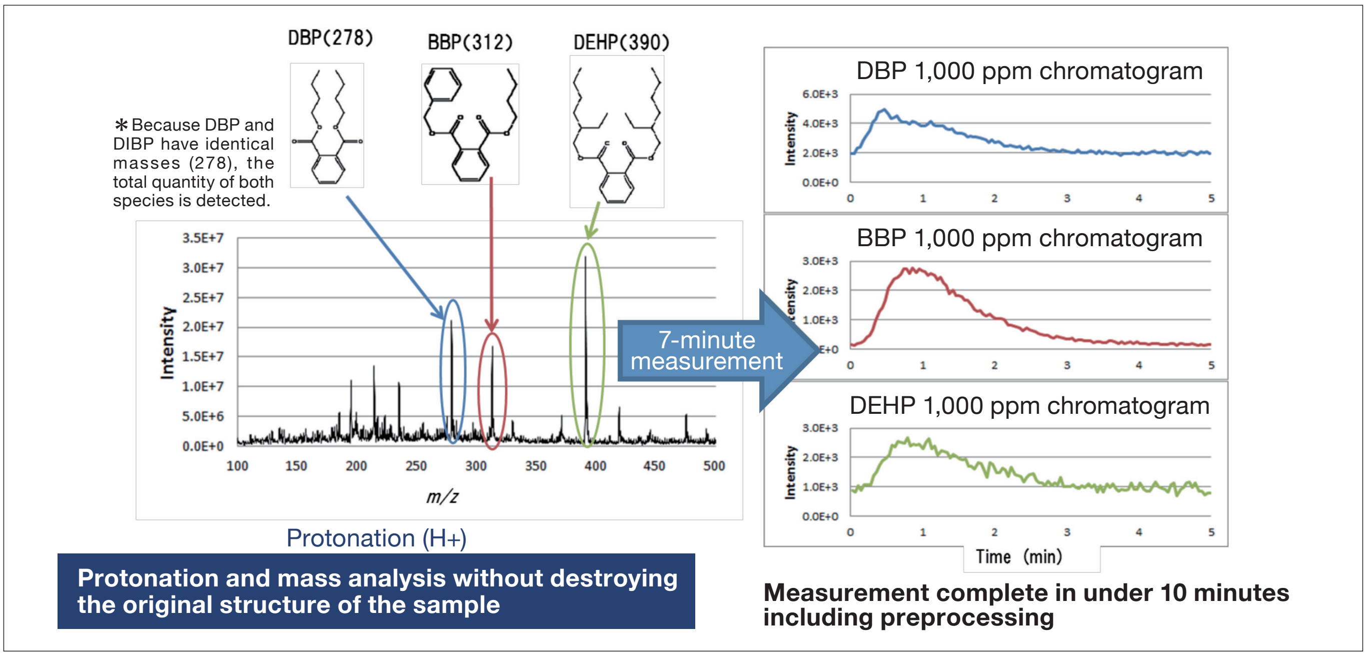

Fig. 6 Sample measurement of DBP, BBP, and DEHP content of polystyrene

5. Efforts to Reduce Content of Restricted Substances

At BROTHER INDUSTRIES, we test samples for content of the 4 types of phthalates in accordance with the BROTHER GROUP GREEN PROCUREMENT STANDARD[4]. However, in view of the risk that phthalates may be transferrable—that is, that they may be transmitted from one article to another via contact between the articles—it has been noted that phthalates could be introduced into the manufacturing process due to unintentional external factors such as migration, blending, or contamination[5]. For this reason, it is necessary to test all components suspected to contain phthalates.

With the objective of facilitating efficient and accurate screening, BROTHER INDUSTRIES and Hitachi High-Tech Science have conducted tests to compare the screening performance of the newly developed screening instrument against that of the solvent-extraction method and that of the gas-chromatograph mass analysis following conventional thermal desorption or pyrolysis; the results are shown in Table 4.

A comparison of data obtained with the phthalate screening instrument developed by Hitachi High-Tech Science versus data obtained via the conventional method of solvent extraction and gas-chromatograph mass analysis confirms that both techniques are comparable and may be used as screening methods.

One other important finding emerges from this comparison. The phthalate DEHP is present in large quantities—tens of thousands of ppm—in the resin-mold specimen. On the other hand, the electric wire sheath specimen—whose flexibility is similar to that of the resin-mold specimen—contains DEHP at levels below the regulatory threshold of 1,000 ppm established by the EU RoHS directive. For the measurements involved in this example, outsourcing the solvent-extraction gas-chromatograph mass analysis to an external testing organization would involve a delay of several days before obtaining results, due to the operational burden of the solvent-extraction method. In contrast, the phthalate screening instrument developed by Hitachi High-Tech Science can measure a single sample in under 10 minutes and produced results for these measurements within 20 minutes, demonstrating the extreme usefulness of this instrument for deployment at manufacturing sites.

Compliance with the EU RoHS directive requires that content of restricted substances lie below regulatory thresholds in physically separable units of uniform materials. At BROTHER INDUSTRIES, we take care to ensure compliance not only by maintaining test data for green procurement but also by using a fluorescence X-ray analyzer to screen for levels of the elements cadmium, lead, mercury, chrome, and bromine. In the future, we are convinced that the use of Hitachi's phthalate screening instrument in conjunction with efforts to reduce levels of substances subject to new EU RoHS regulations will contribute significantly to helping ensure compliance with these new regulations.

Table 4: Comparison of screening methods

Subject of measurement: DEHP (Figure 7)	Hitachi High-Tech Science phthalate screening instrument(＊1)	Gas chromatograph mass analysis following preprocessing via solvent extraction(＊2)	Gas chromatograph mass analysis following conventional thermal desorption or pyrolysis (＊2)
Resin mold	≥40,000 ppm	64,000 ppm	≥1,500 ppm
Electric wire sheath	213 ppm	89 ppm	500 - 1,500 ppm

(＊1) Measurement results obtained by Hitachi High-Tech Science
(＊2) Measurement results obtained by an external analysis organization retained on a contractual basis

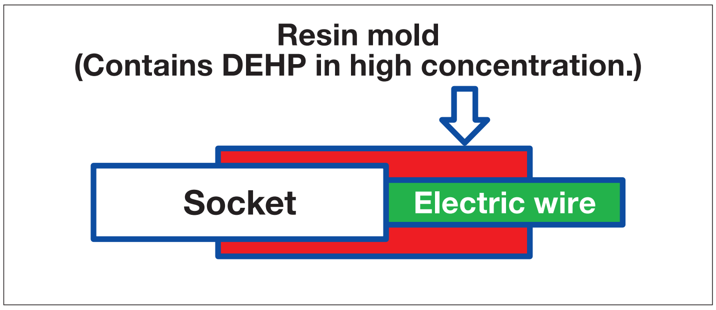

Fig. 7 Schematic diagram of sample specimens

6. Anticipating Future Regulatory Activity

In the EU, the Sweden Chemicals Agency (KemI) has proposed medium-chain chlorinated paraffin (C14-C17, known as MCCP) as a substance to be restricted under the next EU RoHS directive. A report arguing that “MCCP should be restricted by RoHS” has already been publicly released[6], and it is possible that new additions to the EU RoHS dossier of restricted substances will be announced in the near future. As this example indicates, the scope of restrictions on chemical substances has begun to expand from single compounds to entire groups of substances that include molecules spanning a complicated range of masses. The screening instrument developed by Hitachi High-Tech Science directly ionizes the sample and uses a mass analyzer to study the resulting products as they are, without further modification. Consequently, even when making measurements of groups of substances that include molecules spanning a complicated range of masses, the instrument offers the promise of measuring individual components—and thus the possibility of being adapted for use in measuring new types of substances in the event of expanded regulatory restrictions in the future.

7. Conclusions: Key Advantages of the New Screening Methodology

In this section, we summarize the key advantages of the Hitachi High-Tech Science phthalate screening instrument and the methodology it facilitates.

(1) Effectiveness in reducing environmental impact (including CO_2 reduction)

As discussed in Section 3, phthalates serve as plasticizers and are used for a variety of purposes. The 4 types of phthalates whose use will soon be restricted by the EU RoHS directive are included on the list of candidate substances for authorization as articles under EU REACH regulations, which must be submitted by the importers responsible for importing over 1 ton of these substances per year into the EU. In addition, the use of the three substances, DBP, BBP, and DEHP (though not DIBP), in toys or products for child care has been banned in all countries, indicating a global awareness of the risks of human ingestion of these chemicals. The establishment of the screening system discussed in this report for 4 types of phthalates will help to reduce the content of these substances in electrical and electronic products around the world, an enormously effective step in reducing environmental burden. In addition, the screening instrument discussed here does not require solvent extraction and thus does not make use of large quantities of organic solvents during analysis, further enhancing its role in reducing environmental burden.

(2) Technological novelty

BROTHER INDUSTRIES and Hitachi High-Tech Science keep abreast of current trends—including acquiring information on new substances added to the EU RoHS directive—by participating in industrial societies and through other means, and have strived to respond to the latest regulations governing content of chemical substances. The information that the EU RoHS would ban 4 types of phthalates—and that the use of these chemicals in electrical and electronic products brought to market in the EU would be restricted as of July 22, 2019—was announced in an official communication dated June 4, 2015; the fact that we had already begun to research these matters before the official announcement testifies to the timeliness of the projects we pursue. (Restrictions on the use of phthalates in medical devices and monitoring and control instrument will go into effect on July 22, 2021).

Against this backdrop, the HM1000 phthalate screening instrument developed by Hitachi High-Tech Science, which became available for purchase on July 13, 2017 and which boasts advantages including rapid measurement times (less than 10 minutes for a single sample), low purchase cost (compared to conventional gas-chromatograph mass analyzers based on thermal desorption or pyrolysis), and low operating costs (because the instrument does not need helium gas or chromatography columns, and can analyze up to 50 samples continuously), is an instrument ready for deployment at manufacturing sites around the world and thus a demonstration of extraordinary technological novelty.

(3) Effectiveness in reducing energy consumption

The newly developed phthalate screening instrument uses nitrogen gas and does not use the helium gas typically required by conventional mass analyzers. Because nitrogen gas is present in abundance in air, there is no need to supply nitrogen gas canisters when operating the instrument.

Thus, by developing a phthalate screening instrument designed to operate on nitrogen gas, Hitachi High-Tech Science has made a crucial contribution to slowing the depletion of global helium-gas resources.

Helium gas is produced around the world as a byproduct of natural gas, but the U.S. produces over 70% of the global supply, with export restrictions imposed by U.S. government policy. Meanwhile, the properties of helium gas make it an essential precious resource for medical and industrial applications. The world experienced a shortage of helium gas between 2012 and 2013, and some facilities in Japan were among those unable to secure a stable supply. Avoiding the use of precious helium gas for analytical purposes—and instead using nitrogen gas, which may be separated and purified from air—affords an incalculable reduction in the consumption of energy used to produce helium gas.

Since 2006, fluorescence X-ray analyzers have been used as screening instruments to comply with the EU RoHS directive. According the 2010 White Paper on Manufacturing Industries—an annual report prepared in accordance with Article 8 of Japan’s Basic Act on the Promotion of Core Manufacturing Technology—domestic Japanese sales of fluorescence X-ray analyzers reached 1,000 units in FY2008[7). Assuming that the imposition of new restrictions on chemical substances results in the yearly installation of a similar number of phthalate screening instruments, a simple calculation yields an estimate of 84,000 m^3 of helium gas used for analytical purposes (see Table 5 for information on helium gas usage). This corresponds to approximately 0.8% of Japan’s total imports of 11,000,000 m^3 of helium gas[8)] in FY2013.

The gas-chromatograph mass analyzers that have been used in the past require an essentially continuous flow of helium gas while in operation. Consequently, if global use of gas-chromatograph mass analyzers were to increase, the world might again face the problem of helium-gas shortages. Thus, avoiding the use of the precious resource of helium gas reduces not only energy consumption but also the depletion of the Earth’s natural resources.

(4) Highly general and extensible technology

Restrictions on chemical substances become more stringent with each passing year, and—as noted in Section 6—have begun to expand in scope from single compounds to entire groups of substances that include molecules spanning a complicated range of masses. Separation via gas chromatograph has the advantage of being able to separate molecules of identical masses, but also the drawback of producing overly complicated peaks, complicating the identification of specific carbon chains. However, the use of a mass analyzer alone—the approach adopted by the instrument discussed in this report—to study a sample of, say, chlorinated paraffin offers the promise of identifying short chains (C10-C13) and medium chains (C14-C17) by obtaining the ion peaks for each carbon chain, as well as the potential to extend the range of screening technology to other difficult-to-separate compounds. In addition, the instrument may be used to perform automated analysis simply by mounting 0.2 mg quantities of samples, and merely identifying molecular ion peaks suffices to determine constituent components; thus the instrument may be operated even by users without expert-level expertise in chemical analysis, testifying to its extremely high generality.

(5) Effectiveness in reducing costs

The instrument discussed in this report consists solely of a pyrolysis unit and a mass analyzer, with no need for a gas chromatograph. These factors—as noted above in our discussions of items (2) ("Technological novelty") and (3) ("Effectiveness in reducing energy consumption")—serve to reduce both the cost of the instrument (as compared to that of a gas-chromatograph mass analyzer based on conventional thermal desorption or pyrolysis) and the cost of operating it (by avoiding the need for helium gas and chromatography columns and allowing continuous analysis of up to 50 samples) (Table 5).

(6) Other factors

The instrument discussed in this report is equipped with data-import functionality to allow users to enter specimen tables containing information on measurement samples. As a result, sample information may be shared with the phthalate screening instrument by using it in conjunction with a fluorescence X-ray analyzer, the use of which has been part of compliance with the EU RoHS directive since 2006. Moreover, whereas users of fluorescence X-ray analyzers were restricted to detecting information on elements, the new techniques reported here make it possible to envision measuring Deca-PBDE, a particular bromine-based flame retardant.

Thus, using the techniques of this report together with conventional fluorescence X-ray analyzers not only reduces the work required to make measurements, but also offers the enormous advantage of facilitating a comprehensive, unified approach to compliance with the full catalog of chemical-substance content restrictions mandated by the EU RoHS directive (Figure 8). Moreover, the ability to investigate various approaches to ensuring compliance with future regulations gives manufacturers the peace of mind of knowing they will be able to continue providing customers with safe products—a feature that is perhaps the single greatest advantage of the screening methodology discussed in this report.

Table 5: Cost comparison

	Hitachi High-Tech Science phthalate screening instrument	Gas chromatograph mass analyzer using conventional thermal desorption or pyrolysis
Preprocessing + measurement time	10 min / sample	Approximately 40 min / sample
Number of measurements per day (assuming 24 hours per day)	144 samples	36 samples
Autosampler	50 samples (8 hours of continuous measurement)	48 samples (32 hours of continuous measurement)
Gas used for analysis	Nitrogen gas (no need to supply in canister form; simply use nitrogen production equipment)	Helium gas
Gas and other operating costs per 1 year of operation (per unit)	Electric bills only	Helium gas: 7 m^3 43,000 yen × 12 = 516,000 yen (84 m^3) (Typical price in Japan)

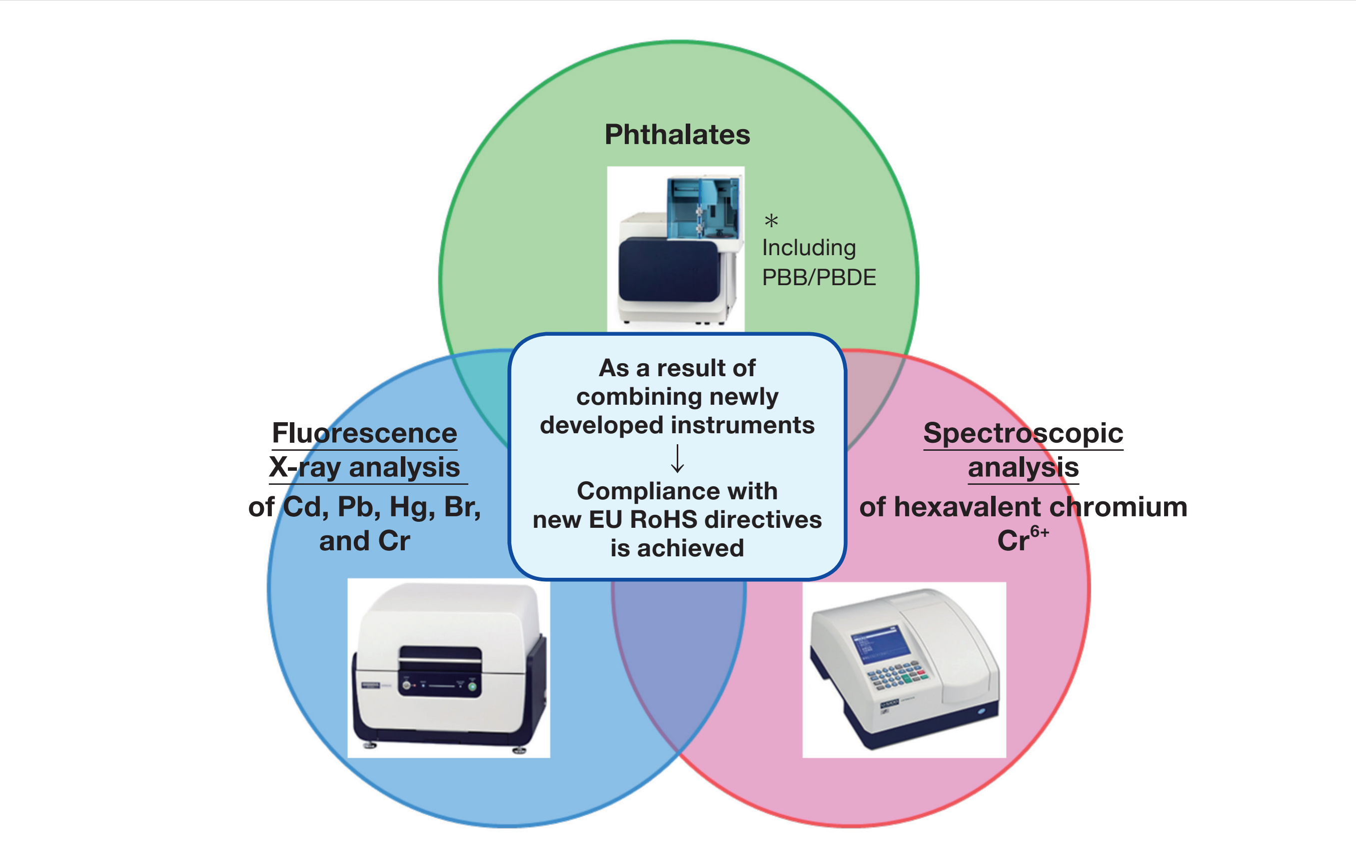

Fig. 8 Schematic illustration of comprehensive approach to compliance with RoHS directive enabled by analytical instruments from Hitachi High-Tech Science

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