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Novel gas chromatography–mass spectrometry database for automatic identification and quantification of micropollutants

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Abstract

A novel gas chromatography–mass spectroscopy (GC–MS) database for identification and quantification of micropollutants in environmental and food samples is reported. GC retention times, calibration curves, and mass spectra of nearly 700 chemicals were registered in the database, and the GC retention times of registered chemicals in actual samples were predicted from the retention times of *n*-alkanes measured before sample analysis. Differences between predicted and actual retention times were less than 3 s, an accuracy that is nearly identical to that obtained by analysis of standard substances. After the retention times were predicted, a calibration file for the GC–MS instrument was created from the predicted retention times, calibration curves, and mass spectra of the registered chemicals. With the resulting calibration file, automated identification of all the chemicals in actual samples was possible without the use of standards, and the identification method was as reliable as conventional methods. When the GC inlet, column, and tuning conditions were adjusted using GC–MS performance check standards, relative standard deviations of 20% or less for determination values could be obtained. More than 90% of the chemicals in the database could be detected at a sensitivity sufficient for all practical purposes (100 pg or less). Because each chemical in the database, to which new substances can easily be added, can be determined in 1 h, micropollutants in samples can be analyzed efficiently and inexpensively.

Keywords: Retention time; Mass spectrum; Simultaneous analysis; Hazardous chemicals; Comprehensive analysis

1. Introduction

More than 70,000 chemicals are currently in use, and the amounts and types of chemicals being produced have been rapidly increasing [1]. Various adverse effects, both expected and unexpected, have been reported for many chemicals [2]. To take appropriate countermeasures against these effects, it is first necessary to determine the levels of chemical pollutants in the environment, in foodstuffs, and so on. Toxic chemicals are monitored or surveyed in many countries, and gas chromatography–mass spectroscopy (GC–MS) is the most frequently used analytical technique because of its high sensitivity, selectivity, and flexibility, even for monitoring trace amounts of chemicals. However, before actual samples can be tested, standards of target substances must be analyzed for the determination of retention times and the preparation of calibration curves, which are often affected by subtle differences in GC–MS conditions. The necessity for standards restricts the number of chemicals that can be simultaneously analyzed by GC–MS; at the present time, that number seems to be on the order of hundreds.

We developed an analytical method that can simultaneously determine 300 substances by means of GC–ion trap MS [3]. In experimenting with the method, we observed that exact retention times are essential for correct identification of targets; standard substances must be analyzed for exact retention times; and preparing all 300 standards before sample analysis is costly and time consuming. We also discovered that quantification results for the standards do not

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vary unexpectedly as long as the GC–MS conditions are kept constant.

On the basis of these observations, we have developed a new combined database for GC–MS to overcome some of the limitations of traditional GC–MS analysis [4]. The database actually consists of three databases—mass spectra, retention times, and calibration curves—all of which are essential for both identification and quantification of target substances. As long as the GC–MS conditions remain constant, the database system can be used to predict exact retention times and to obtain reliable quantification results without prior analysis of standards. In addition, new substances can be easily added to the database. Therefore, any chemical to which the specified GC conditions are applicable can be analyzed by means of the system. Moreover, if similar databases were constructed using different GC conditions, it would theoretically be possible to analyze, without standards, most of the chemicals to which GC is applicable.

In the previous report [4], we (1) demonstrated the effectiveness of GC–MS performance check standards (PCS) for evaluation of GC–MS performance and maintenance of the instruments, (2) described a method for predicting retention times, (3) accurately and precisely predicted retention times with a single instrument, (4) correctly identified and quantified chemicals with a single instrument, and (5) evaluated the identification and quantification performance of the method using spiked samples with a single instrument.

Our first objective in the present study was to investigate how the correctness of predicted retention times varied when several instruments manufactured by one company were used and when an instrument manufactured by a different company was used. We also evaluated the identification performance of the database system by comparing it to the automated mass spectral deconvolution and identification system (AMDIS) [5], which is one of the best mass spectral search systems available. Our second objective was to investigate variations in quantification results with different instruments and at different times, which is a key determinant of the database system's flexibility. Our third objective was to confirm the effectiveness of the database for analyzing actual samples.

2. Experimental

2.1. Reagents

Chemicals registered in the database and GC–MS performance check standards were obtained from commercial suppliers. The internal standard mixture (Table 1) and the *n*-alkane (*n*-C_9H_{20} to *n*-$C_{33}H_{68}$) mixture were obtained from Hayashi Pure Chemical (Osaka, Japan). Standard solutions for calibration curves were prepared by adding 1 μg of each internal standard to 1 mL of a hexane solution containing designated amounts of the target chemicals (0.01, 0.1, 1, or 10 μg). A PCS solution (Table 1; 1 μg of each compound in 1 mL of hexane) was prepared in the same way as standard solutions of the chemicals.

2.2. Instruments and conditions

A Shimadzu QP-2010 GC–MS (Shimadzu Corporation, Kyoto, Japan) with a J&W DB-5 ms capillary column (Agilent Technologies, San Jose, CA, USA) was used for construction of the database and for sample analysis. The GC–MS conditions have already been reported [4]. An Agilent 6890 GC/5973 MSD instrument (Agilent Technologies) was used to evaluate the retention time prediction performance and quantitative performance of the database system;

Table 1
Internal standards and performance check standards for GC–MS

Internal standards		
4-Chlorotoluene-d_4, 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Phenanthrene-d_{10}, Acenaphthene-d_{10}, Fluoranthene-d_{10}, Chrysene-d_{12}, Perylene-d_{12}		
Performance check standards		
Chemicals	Check items	Criteria
Decafluorotriphenylphosphine (DFTPP)	Spectrum validity	Mass spectrum of DFTPP should meet the mass intensity criteria of EPA Method 1625
trans-Nonachlor		Mass spectrum of nonachlor should be the same as that of standard
Benzidine, pentachlorophenol	Inertness of GC column and inlet liner	Benzidine, pentachlorophenol, and 2,4-dinitroaniline should be present at their normal responses, and extreme peak tailing should not be visible
4,4′-DDT	Inertness of GC inlet liner	Degradation of DDT to DDD should not exceed 20%
25 *n*-Alkanes (*n*-C_9H_{20} to *n*-$C_{33}H_{68}$), *n*-octanol, 2,4-dichloroaniline, 2,6-dichlorophenol, Tris(2-chloroethyl)phosphate, decafluorotriphenylphosphine, benzothiazole, 2,4-dinitroaniline, benzidine, *trans*-nonachlor, 4,4′-DDT pentachlorophenol, 2,4,6-trinitrotoluene	Stability of response	Determined amounts of these compounds should fall within 95% confidence limits of the mean values

the GC–MS conditions for this instrument were the same as those for the Shimadzu instrument.

2.3. Construction of the database

The database system consists of the database, which was created with Microsoft Access, and two interface software programs: Software A (trade name: Compound Composer – database registration phase) transfers retention times, mass spectra, and calibration curves in the calibration files of the GC–MS instrument to the database; Software B (trade name: Compound Composer – method creation phase) creates calibration files for the GC–MS instrument from the database. After the GC–MS conditions were set, target tuning to meet the criteria for EPA Method 625 [6] was performed. Then the PCS solution was measured, the retention times of *n*-alkanes were confirmed, and GC–MS performance was determined by evaluating the analytical results in terms of the criteria in Table 1. If all the criteria were met, standard solutions of a chemical were measured for preparation of a calibration curve. Then, a calibration file for the chemical, which consisted of mass spectrum, retention time, quantification ion, calibration curve, and so forth, was created according to the conventional method. Finally, the calibration file data and the retention times of two *n*-alkanes between which the retention time of the chemical fell were registered in the database with Software A. Currently, 672 compounds, including 332 pesticides, are registered (Table 2). These chemicals are known to adversely affect human health, the environment, or both. We selected the chemicals from lists of compounds regulated by environmental protection laws in Japan or the United States and from lists of chemicals detected in environmental surveys by the Japanese Ministry of the Environment [7]. In addition, we registered many pesticides because a positive list system, which prohibits the use of pesticides that are not registered on the list, will be introduced for agricultural chemical residues in food in 2006 in Japan.

2.4. Measurement of chemicals in samples using the database system

The GC–MS spectrum of the PCS solution was measured under the conditions used for database construction, and the results were evaluated against the criteria in Table 1. When the PCS results satisfied the criteria, a 1 μL aliquot of sample solution containing internal standards was injected into the GC–MS instrument. On the basis of the retention times of the *n*-alkanes both from the PCS analysis and in the database, retention times of all the targets were predicted; then the calibration file, which consisted of the predicted retention times, mass spectra, and calibration curves, was created from the database with Software B. The targets were identified and quantified by means of the created calibration file; this procedure is the same as that used for ordinary GC–MS analysis.

Fig. 1 shows a screenshot of the data for an orange extract. On the basis of the data, we concluded that α-HCH was present in the extract, because two conditions were met: (1) the GC trace showed a peak for the quantification ion (*m*/*z* 219) of α-HCH, and the retention time (20.626 min) of the peak fell within the range (±0.05 min) that included the predicted retention time (20.617 min); and (2) the similarity value (93; obtained by a reverse search technique) between the mass spectrum of the peak and that of the target chemical in the calibration curve was larger than a default value (65). The amount of α-HCH (0.2175 μg) was calculated using the peak intensity ratio of the quantification ion (*m*/*z* 219) and the corresponding internal standard (phenanthrene-d_{10}, *m*/*z* 188) and a calibration curve recorded in the calibration file. These identification and quantification cycles were repeated until the last substance in the calibration file had been identified. Because 1 h each was required to analyze the PCS solution and one sample, results for the first sample were obtained after 2 h. After this initial period, results for each subsequent sample were obtained in 1 h. However, since the database system does not include pretreatment of samples, the analyst has

Table 2
Types of chemicals registered in the database

Class 1	Number	Class 2	Number
Chemicals consisting of C and H	160	Polycyclic aromatic hydrocarbons	49
		Polychlorinated biphenyls	62
		Other	49
Chemicals consisting of C, H, and O	81	Phenols	48
		Other	33
Chemicals containing N	85	Aromatic amines	36
		Nitro compounds	36
		Other	13
Chemicals containing S	8		8
Chemicals containing P	6		6
Pesticides	332	Insecticides	137
		Herbicides	92
		Fungicides	80
		Other	23
Total	672		

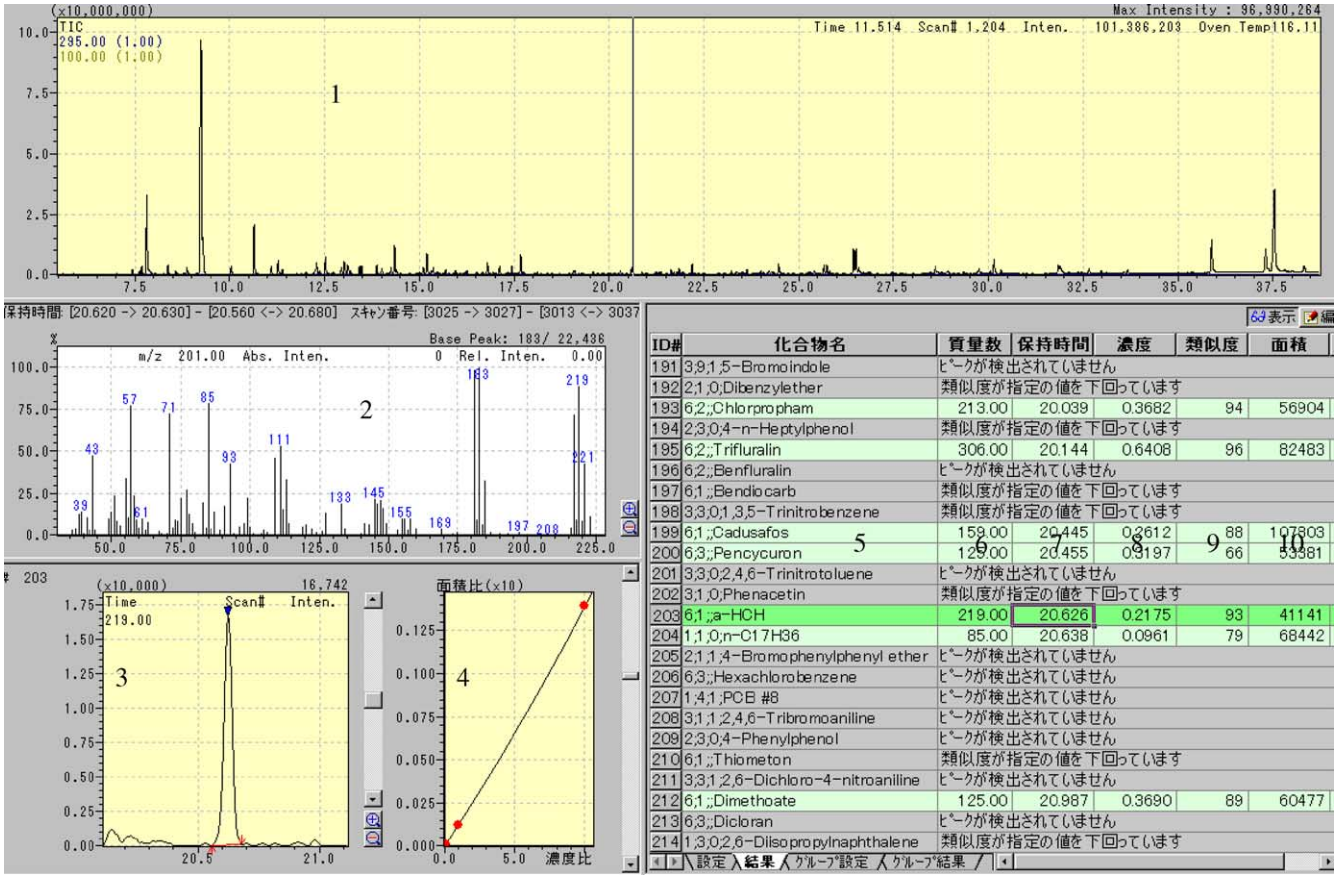

Fig. 1. Screenshot of analytical data for an orange extract. α-HCH was detected. (1) Total ion chromatogram; (2) mass spectrum of a target chemical; (3) mass chromatogram of the quantification ion of the chemical; (4) calibration curve of the chemical; (5) name of the chemical; (6) mass number of the quantification ion; (7) retention time; (8) detected amount; (9) similarity value for the mass spectrum and (10) peak area.

to pretreat samples appropriately to obtain correct analytical results.

3. Results and discussion

In GC–MS analysis, retention times, mass spectra, and calibration curves of target chemicals are essential for both identification and quantification, and these data are registered in calibration files. But because retention times and calibration curves are often affected by GC–MS conditions, such as the carrier gas flow rate and the inertness of the GC inlet liner and column, standards for targets compounds should be measured to confirm retention times and calibration curves before sample analysis. Since this procedure is time consuming and costly, the number of targets that can be analyzed by GC–MS is restricted. The database system we have developed will enable analysts to detect and identify many chemicals efficiently and inexpensively. However, correct results can be obtained only when the GC–MS is maintained appropriately, that is, when the GC–MS conditions used to analyze samples are the same as those used to construct the database.

To obtain correct analytical results, we used a PCS solution to predict retention times, tune the target mass, and evaluate the performance of the GC–MS system. Several criteria for evaluating the inertness of capillary columns and inlet liners have been published [6,8]. We designed our PCS solution and evaluation criteria on the basis of our own experiments and published criteria for evaluating the inertness of capillary columns and inlet liners [6,8]. The chemicals in the PCS solution and the relevant evaluation criteria are shown in Table 1. As long as the analytical results for the PCS solution met the criteria, we considered the GC–MS performance to be nearly the same as that used to construct the database, and therefore we expected the database system to provide reliable results.

3.1. Accuracy of predicted retention times

The retention time prediction method and the accuracy of predicted retention times using a single instrument have been discussed in detail in a previous report [4]; the differences between predicted and actual retention times were less than 3 s. In the present study, the accuracy and precision of the predicted retention times for the PCS were investigated under the designated GC conditions using multiple columns and multiple GC–MS instruments, including an instrument made by a different manufacturer (Agilent 6890 GC/5973 MSD). In all cases, the differences between predicted and actual

retention times were less than 3 s, which indicates that the method can be used to accurately predict retention times as long as the designated GC conditions are used.

Establishing the designated GC conditions is not difficult, except with regard to column length; usually a column must be cut. When the column length was changed, the accuracy of the predicted retention times was still good as long as the same linear velocity, 40 cm/s, was used. However, we occasionally observed unexpected variations due to differences in the film thickness of the stationary phase and/or the internal diameter, even with a new column. We compensated for these variations by increasing the column head pressure from the initial pressure to 0.669 psi per 1 s delay of perylene-d_{12} to obtain correct predicted retention times.

The injection solvent and sample matrix also affected retention times. Because the solvent used to construct the database was hexane, using a solvent with a boiling point higher than that of hexane increased the retention times of chemicals relative to the predicted times. The difference seemed to be caused by the solvent effect. We solved this problem by measuring *n*-alkane solutions prepared with the same solvent as that of a sample extract.

Changes in retention times due to the same mechanism as the solvent effect were observed when samples containing a large amount of matrix were analyzed. For example, when we analyzed a vegetable sample that had been insufficiently cleaned up and therefore contained a large amount of matrix (which saturated the detector), the retention times of some of the pesticides, such as isophenphos oxon, were longer than the predicted retention times, the largest difference being approximately 10 s. Phosphate esters such as tris(2-chloroethyl)phosphate also exhibited longer-than-predicted retention times, a phenomenon that was easily confirmed by measurement of a PCS solution. In these situations, we used one of two measures to avoid false negatives: we expanded the search period or carried out additional clean-up procedures. Since expansion of the search period increases the chance of false positives, the use of additional clean-up procedures is recommended. By using additional clean-up procedures for the vegetable sample, we were able to decrease the difference between predicted and actual retention times to less than ±3 s.

3.2. Correctness of identification

Because many chemicals are registered in the database, false negatives are difficult to avoid. Both high-quality mass spectra and correct retention times are essential for reducing the chance of false negatives. Although high-quality mass spectra are rarely obtained in actual environmental samples because hazardous substances in such samples are usually present at very low concentrations, the retention time prediction method can correctly estimate retention times as long the GC conditions are identical to those used to prepare the database. In addition, we narrowed the search range as much as possible, to 3 s.

In the previous study, we found that reverse searching is more effective than forward searching to identify coeluting substances [4]. Therefore, we used the combination of a reverse search and a narrow search range to detect target substances.

Because AMDIS is one of the most powerful software programs for analysis of GC–MS data, we compared the performance of our database system with that of AMDIS using various samples (Table 3). We prepared a target database for AMDIS that contained most of the chemicals registered in our database. Both identifications procedures were performed with a set of default values for parameters.

When the concentrations of the targets were high and the quantity of matrix was low, such as in the water and soil samples (Table 3), automated identification of all the spiked substances could be performed correctly. However, some of the spiked substances in the spinach and orange samples, which contained a large amount of matrix, could not be identified automatically (there were false negatives). False negatives were also observed in the sediment samples. Because

Table 3
Comparison of the identification performance of the database system and AMDIS[a]

Sample	Number of spiked chemicals	Detected number		Number of false negatives		Number of false positives	
		Database system	AMDIS	Database system	AMDIS	Database system	AMDIS
River water[b]	13	13	12	0	1	0	0
Soil[c]	56	56	51	0	5	0	1
Spinach[d]	150	117	82	33	68	0	4
Orange[d]	150	138	101	12	49	0	6
Sediment A[e]	88[f]	57	33	32	59	1	4
Sediment B[e]	68[f]	46	24	22	46	0	2

[a] Chemicals in river water, soil, spinach, and orange were identified automatically using default values for identification parameters.
[b] One microgram of each chemical was added to 1 mL of the concentrate obtained by extraction of 1 L of water with CH_2Cl_2.
[c] One microgram of each chemical was added to 1 mL of the concentrate obtained by silica-gel column chromatography of an extract from 20 g of soil.
[d] After the addition of 0.1 μg of each pesticide to 2 g of each sample, pretreatment involving supercritical fluid extraction and silica-NH_2 and carbon graphite cartridge column chromatography was performed.
[e] After the extraction of 50 g of a sample with acetone, the extract was added to water and extracted with CH_2Cl_2, and then sulfur was removed with a copper powder.
[f] Chemicals were manually identified.

the sediment samples were raw extracts (the only clean-up procedure was sulfur removal with a copper powder), the extracts contained a lot of matrix. These results showed that automatically identifying all chemicals in a dirty sample is difficult. However, in these cases, the analyst can determine whether a target is present by manual identification, as long as a quantification ion peak appears at the predicted retention time, as in Fig. 1. Chemicals in sediments in Table 3 were found in this way.

The numbers of both false negatives and false positives were higher for AMDIS than for our database system. However, we did not use retention time data in the AMDIS system; if the AMDIS database had contained retention time data, the number of false positives may have been reduced. The reason that the identification performance of our database system was better than that of AMDIS seems to be the difference in the search direction. The database system determines whether a peak for a registered chemical is present at the prediction retention time in the TIC, whereas AMDIS determines whether a chemical found in the TIC exists in a database, such as the NIST database. Therefore, combining the database system with AMDIS may synergistically improve identification performance.

3.3. Accuracy and precision of quantification

The most difficult task for our database system was to obtain correct quantification results with any GC–MS instrument. Several factors affect the quantification of chemicals: the nature of the column and the inlet liner and the tuning of the MS. EPA Method 625 uses system PCS to evaluate the influence of these factors [6]. The analyst can relatively easily control the performance of the column and the inlet liner, but evaluating and controlling the tuning performance are difficult. However, tuning affects quantification results because the database system quantifies concentrations of chemicals by the internal standard method using peak areas of quantification ions of a chemical and an internal standard obtained in the scanning mode. If a fragment pattern of a chemical at the time of sample analysis differs from that of the chemical in the database, correct quantification results of the chemical are not obtained. Therefore, we examined the reproducibility of tuning under various conditions using decafluorotriphenylphosphine (DFTPP). We used DFTPP to minimize effects other than tuning and because the GC–MS used in our study had a tuning method for DFTPP. We obtained peak intensities of fragment ions of DFTPP from PCS analyses with one GC–MS instrument, and we set the peak intensity ratio of each fragment ion with respect to the intensity of the base ion (m/z = 198) to 1. Then we analyzed the PCS solution with six instruments, obtained fragment intensities for DFTPP, and compared those intensities to the ratios, which were set to 1 (Table 4). Five fragment ions showed good reproducibility: their means were close to 1, and their relative standard deviations (RSDs) were below 10%. These ions were high-intensity ions or were close to m/z 198. The remaining ions, which were low intensity or far from m/z 198, had higher RSDs. Because the quantification ion intensities of both the target substance and an internal standard affect a quantification result, in the worst case, a quantification result will have an RSD of 50%. In order to reduce the high RSD, improvement of the reproducibility of tuning among different instruments is needed.

Table 4
Reproducibility of intensity ratio of fragment ions relative to the intensity of m/z 198 of decafluorotriphenylphosphine

m/z	Mean ratio	SD	RSD (%)
51	1.18	0.21	17.7
77	1.07	0.10	9.5
110	1.02	0.09	8.5
127	1.01	0.09	9.0
167	1.20	0.20	16.8
186	1.10	0.11	9.7
224	0.96	0.08	8.6
255	0.89	0.11	11.9
275	0.83	0.16	19.4
296	0.89	0.14	15.8
323	0.94	0.14	15.1
365	0.98	0.25	25.1
423	1.34	0.34	25.1
442	1.20	0.23	19.3

Mean ratio: the ratio of the intensity of each fragment ion to that of m/z 198, which was obtained with one GC–MS instrument, was set to 1; the reproducibility of the intensity ratio of each ion to m/z 198 was calculated using the data obtained with each of the six GC–MS instruments; SD: standard deviation; RSD: relative standard deviation.

Next, we analyzed the PCS solution to determine the overall effect of the different instruments on the accuracy and precision of quantification. We carried out three experiments: the first was performed using four columns and a Shimadzu GC–MS; the second used one column and five Shimadzu GC–MS instruments; and the third used one column and an Agilent GC–MS (Fig. 2). In the first and the third experiments, the GC–MS performances met the criteria in Table 1. In the second experiment, however, the spectrum validity for DFTPP was the only criterion that was met. In the first test, all the chemicals—except for highly polar compounds, such as pentachlorophenol, benzidine, and 2,4-dinitroaniline—could be determined accurately; the mean value and the mean RSD were 1.06 ng and 9.0%, respectively. These results were not markedly worse than the results obtained by the conventional internal standard method, which indicates that if GC–MS performance satisfies the criteria in Table 1, common chemicals can be determined with a high reliability even with different columns.

The analytical results of the second experiment were worse than those of the first experiment. Quantification results for basic substances were low; in particular, benzidine was not detected. The cause of the false negative seemed to be that the column conditions were slightly acidic. In addition, the detected amount of *n*-$C_{30}H_{62}$ and the corresponding RSD were very large. Since *n*-alkanes are usually not affected by column conditions, we suspect that improper tuning was the cause of the poor results. Thus, we examined the fragment

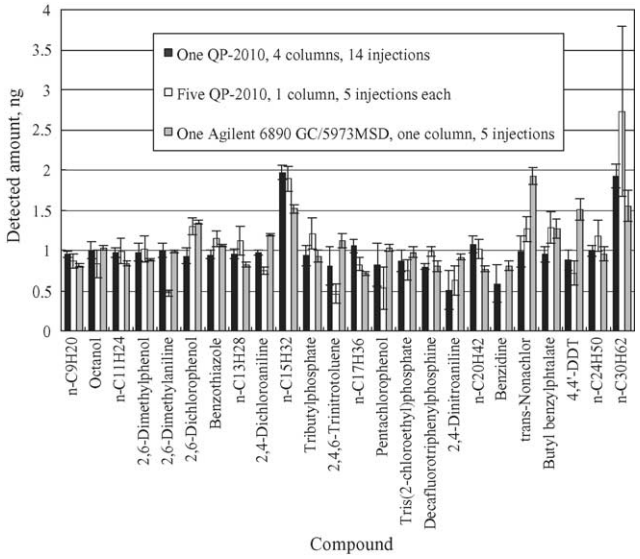

Fig. 2. Reproducibility of quantification results for GC–MS system performance check standards. The injection amount of each chemical was 1 ng, except for *n*-$C_{15}H_{32}$ and *n*-$C_{30}H_{62}$, which were injected at 2 ng.

pattern for DFTPP with each instrument. We found that with two instruments, the intensity of *m*/*z* 77, which is close to *m*/*z* 85 of the quantification ion of *n*-$C_{30}H_{62}$, was larger than usual, whereas the intensities of *m*/*z* 255 and 277, which are close to *m*/*z* 264 of the quantification ion of perylene-d_{12} (which is the internal standard for *n*-$C_{30}H_{62}$), were smaller than usual. Therefore, the high result for *n*-$C_{30}H_{62}$ was due to the fact that the fragment pattern of DFTPP differed from the usual pattern, even though the criteria of EPA Method 625 had been met. This result indicates that a criterion for DFTPP more stringent than that specified by EPA Method 625 is necessary for correct analytical results: increasing the number of evaluation ions and reducing the width of tolerance (e.g., 30–60% of *m*/*z* 198 for *m*/*z* 51), including setting an upper limit (e.g., >40% of *m*/*z* 198 for *m*/*z* 442) or a lower limit (e.g., <2% of *m*/*z* 69 for *m*/*z* 70).

The results of the third experiment, which used the Agilent GC–MS instrument, were nearly equivalent to those obtained with the Shimadzu GC–MS instruments (Fig. 2). This result indicates that if an interface software, such as Software A and Software B for the Shimadzu instrument, for the database and different manufacturers' instruments were created, reliable results could be obtained with any instrument as long as the designated GC–MS conditions were used. Another way to analyze measurement data obtained with different manufacturers' instruments is to convert the data file to an analytical data interchange file (NetCDF file), which can be interpreted by the Shimadzu system.

Finally, we examined the accuracy and precision of quantification results for actual samples, because samples matrices sometimes affect quantification. We used three types of samples: water, soil, and foodstuffs (Table 5). The accuracy and precision for water and soil samples were similar to those obtained by the internal standard method; because clean samples, which contain only small amounts of matrix, do not differ substantially from standard solutions, this result is not surprising. However, the accuracy and precision for food samples were worse than those for water and soil. The poor results seemed to be due to matrix effects and the smaller injection amount, which was 1/10 that of the water and soil samples. Since similar phenomena are often observed in conventional analysis of dirty samples, sufficient clean-up procedures are needed to obtain correct results. To make best use of the features of the database system, however, simple clean-up procedures may be better than complicated ones, as long as satisfactory screening results are obtained.

3.4. Detection limits

The calibration curves registered in the database were prepared at four concentrations: 0.01, 0.1, 1, and 10 μg/mL. As a result, detection limits of 64 and 30% for the registered chemicals were less than 0.01 and 0.1 μg/mL, respectively. These low detection limits are sufficient for ordinary environment and food analyses but not for ultratrace analysis, such as dioxin analysis.

3.5. Application to actual samples

To evaluate the usefulness of the database system, we applied it to various samples, such as environmental water, effluent water, sediments, soils, and foodstuffs. If chemicals

Table 5
Accuracy and precision of quantification results for actual samples

Sample[a]	Number of spiked chemicals	Spiked amount (μg)	Detected number		Detected amount (μg)			RSD (%)
			Database system	Conventional internal standard method	Mean	Maximum	Minimum	
River water	13	1	13	–	0.86	1.2	0.37	26.5
Soil	56	1	56	–	1.14	1.53	0.61	20.3
Spinach[b]	150	0.1	143[c]	147	0.096	0.41	0.007	53.5
Orange[b]	150	0.1	144[c]	146	0.107	0.38	0.012	51.0

[a] See Table 3 for an explanation of the sample pretreatment procedures.
[b] Mean, maximum, minimum, and relative standard deviation (RSD) were calculated from the ratio of analytical results obtained with the database to those obtained by the conventional internal standard method with an Agilent 6890 GC/5973 MSD.
[c] Chemicals were found by manual identification after automatic identification.

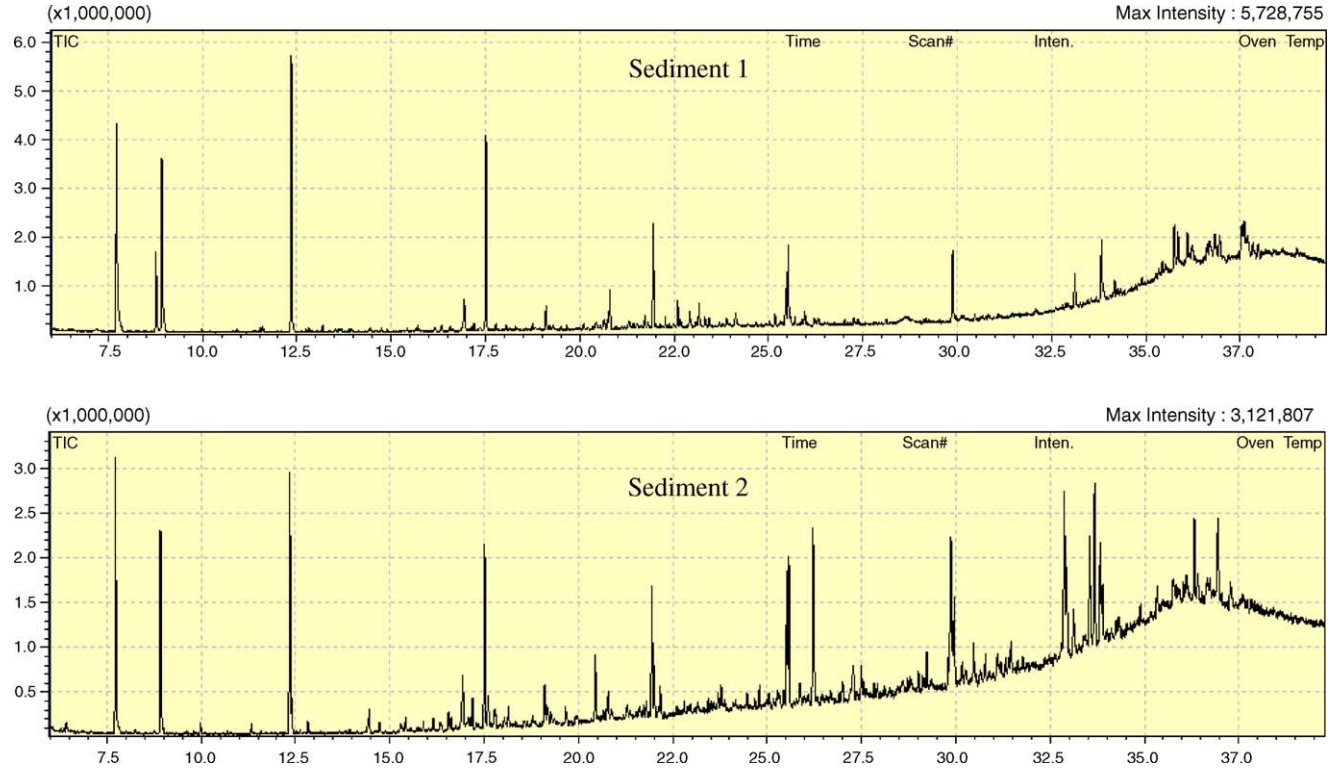

Fig. 3. Total ion chromatograms of sediment extracts. Sediment 1: taken from a tidal flat and sediment 2: taken from a closed sea. See Table 3 for a description of the sample pretreatment procedures.

registered in the database were present in the samples, the chemicals could be accurately identified and quantified. The procedure is easy to perform; no special skills are required. The database system is applicable for various uses, such as confirming the safety of various environmental media or foodstuffs, investigating the causes of environmental pollution incidents, and finding a special feature of environmental pollution by chemicals at a sampling site.

A particular advantage of the database system is that analysts get a comprehensive picture of chemical pollution in samples, which is difficult by conventional methods. For example, we examined two sediments taken from coastal areas around Kitakyushu City, Japan. Sediment 2 was more heavily polluted by chemicals than sediment 1 (Fig. 3), particularly by polycyclic aromatic hydrocarbons; the ratios of the concentrations of all the targets to the concentrations of polycyclic aromatic hydrocarbons in sediments 2 and 1 were 34 and 82, respectively. These advantages of the database system arise from the fact that it can be used to measure a large number of chemicals simultaneously. Although large numbers of substances can also be analyzed by means of many conventional methods, considerable labor, time, and cost are involved.

Even though nearly 700 chemicals are registered in the database, this number is much smaller than the number of chemicals found in the environment, so the current size of the database is insufficient. However, because adding new substances to the database is easy, most of the toxic chemicals to which GC–MS is applicable will be measurable using the database without standard substances in the near future.

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