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Journal of Chromatography A, 974 (2002) 161–168

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

A mass spectral library based on chemical ionization and collision-induced dissociation

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Abstract

A so-called CI–CID mass spectral library based on GC–CI-MS–MS, LC–TSP-MS–MS, LC–ESI-MS–MS and LC–APCI-MS–MS data has been created and evaluated. The main advantage of the CI–CID spectral library is the independence of the chemical ionization and/or collision-induced dissociation procedure and the system apparatus used. Comparison of MS–MS spectra from different ionization methods indicate that fragment ions most often have the same m/z values, although the ratios differ widely for many compounds. Therefore, depending on the signal intensity of the fragment ions the m/z values of intense specific ions are put in the library at 100% and less intense ions at 50%. The result is a spectrum with the same m/z values compared to the acquired spectra but with different ratios. At the moment the library has some hundreds of entries produced at five different laboratories. The spreadsheet program, used to interchange data between laboratories, has full functionality of browsing. Spectra are presented in bar graph format and in tabular form. All input data, instrument configurations, experimental conditions, etc., are displayed. Adding search masses of the (un)known compound, all hits (total number and names) show up. The results of an interlaboratory study show that the CI–CID spectrum library can be used by all users. Comparison of spectra generated by different GC– or LC–MS–MS triple quad mass spectrometers and ion trap MS–MS systems, turned out to be fully comparable.

Keywords: Chemical ionization; Collision-induced dissociation; Mass spectral library

1. Introduction

Today, mass spectrometric detection is increasingly used in LC and GC to improve selectivity and structural information. For GC, huge mass spectral libraries exist with over 300 000 entries. GC–MS has been used worldwide for over 30 years and the ionization is rather constant, that is, the spectrum that is obtained is more or less uniform and unique for a compound. Therefore, the libraries can be used to identify compounds by comparing the unknown spectrum with the spectrum in the library. A spectral match and fit factor defines the certainty of the library search.

For LC, the situation is completely different. Mass spectrometric detection in LC has only become more common the last decade due to the introduction of atmospheric pressure ionization (API) interfaces, i.e., the electrospray and atmospheric pressure chemical ionization interface (ESI and APCI, respectively). Both are soft ionization techniques, comparable with GC–CI-MS, resulting in (de)protonated molecules with little or no fragmentation Therefore, fragmentation is needed to get the additional ions necessary for the identification of compounds. At the moment the

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0021-9673/02/$ – see front matter
PII: S0021-9673(02)01226-8

most common way to achieve fragmentation is collision-induced dissociation (CID). CID can be performed in, e.g., the collision cell of a triple quadrupole, a quadrupole ion trap and also in the source of an atmospheric ionization interface. Unfortunately, the ionization of API interfaces and the fragmentation by CID largely depends on the conditions applied, i.e., the spectra obtained differ widely with the eluent and mass spectrometric conditions applied. Therefore, comparison of a single spectrum of an (un)known compound, normally used with EI, is only useful when all conditions are the same.

Twenty years ago Dawson et al. [1] evaluated the results of a round robin test of EI-CID, with defined conditions. The result was that all spectra were different. A few years later Martinez [2] used fixed settings with an EI-triple quad mass spectrometer to develop a library, i.e., the entries in the library were measurements of compounds generated under the same conditions. In 1995, Josephs [3] used another approach by creating a library based on LC-electrospray-ion-source fragmentation spectra. The CID potential was rotated through different energies on alternate scans throughout the chromatographic run. The spectra across a given chromatographic peak were summed and averaged to give composite spectra, which displayed molecular ions in addition to fragment ions. The spectra were saved into a library. The author demonstrated that, in samples analyzed under the same conditions, the compounds could be recognized after a library search.

Currently, several LC–MS–MS libraries exist. Little [4] and Hough et al. [5] have created libraries based on in-source CID spectra. Hough et al. used the electrospray transport region of a HP1000 MSD instrument. To generate library searchable mass spectra, the instrument was tuned to standard conditions at three offset voltages. The CID library entries were found to be reproducible on other instruments of the same type. Gergov et al. [6] and Slobodnik et al. [7] created libraries based on CID fragmentation in triple quads and used one collision offset voltage to acquire all product ion spectra. Marquet et al. [8] and Weinmann et al. [9] use API libraries of CID fragmentation spectra produced with in-source CID and triple quad MS–MS instruments and use two to four different collision offset voltages for each compound. All spectra were stored as individual library entries. By using glafenine or haloperidol as a tune compound and fixed eluent and ionization conditions, the authors demonstrated that the spectra were reproducible at different laboratories on the same instrument type.

For the ion trap MS–MS instruments, CID libraries also exist. Baumann et al. [10] use a library with about 600 compounds produced with wideband excitation (activation) and normalized collision energies after both APCI and electrospray ionization. The authors claim highly reproducible mass spectra on several LCQ systems, whereas their library can be used as a user library of the NIST library. The use of wideband excitation and normalized collision energy produce mass spectra with more information compared to normal ion trap MS^2 spectra, although many compounds still have a limited number of masses, compared to the number of masses acquired with more MS stages [11,12]

The libraries described above have one thing in common; both, masses and mass ratios are used for identification, a principle that is used in EI libraries too. Using these ''mass/mass ratio'' libraries can only be done by analyzing unknown compounds under the same conditions and on the same type of interface and instrument as used to create the library.

Furthermore, fixed conditions are not always the best way to analyze compounds. Hough et al. [5], Marquet et al. [8] and Weinmann et al. [9] use acetonitrile in the LC eluent. Many compounds show much more sensitivity in LC–MS detection with methanol compared to acetonitrile [13–16], although this effect is instrument dependent. A typical example of a class of compounds that produce often much better S/N ratios in methanol compared to acetonitrile are phenyl urea herbicides. Also different organic modifiers may give different fragmentation ratios caused by different optimum settings.

Schreiber et al. [17] investigated some parameters by creating a library with six to 12 in-source CID spectra for every compound. Each compound was analyzed with APCI and electrospray in both the positive and negative ion mode and fragmented at three different orifice voltages. By changing the eluent and ionization conditions the author demonstrated the possibilities and limitations to use ''mass/mass ratio'' libraries, i.e., based on masses *and* mass ratios.

Bogusz et al. [18] examined the intra- and inter-

laboratory reproducibility of mass spectra of drugs of different polarity on single quadrupole LC–API-MS instruments. The experiments demonstrated that mass spectra of the drugs, obtained in identical conditions with identical instruments, might show very different degrees of fragmentation. Mass spectra obtained on different instruments differed profoundly not only in the degree of fragmentation, but also different fragments and adducts were observed.

In this paper, a mass spectral library for LC and GC is presented for methods which use chemical ionization combined with CID fragmentation techniques. In contrast to the libraries described above, the CI–CID library is produced with fixed m/z ratios, depending on their relative intensity in the acquired spectra and set by the analyst. In this way a universal library is created which all LC and GC systems using CI can use. First the rules how to produce a library entry will be explained, followed by an explanation of the CI–CID library and the results of a round robin test.

2. Experimental

The CI–CID library is developed with a minimum of rules, i.e., to add entries to the library only a few guidelines during analyses and library editing are required in order to meet the goal of the library, that is to be able to search for compounds having specific masses (m/z values).

2.1. Guidelines for analyses to add a library entry

During analysis it is necessary to obtain information of the molecular mass and main fragment ion masses of a compound (Fig. 1). This can be done by applying a series of offset voltages (triple quadrupole, in-source CID) or by applying several MS–MS stages in an ion trap MS. In principle, the offset voltages and the number of MS–MS stages are not important, however, the more masses of a compound are available, the better the final result will be.

Isotopic mass information is important. Isotopes can be acquired in in-source CID and with a triple quad with the first quadrupole at a low resolution. Also MS conditions that are not capable of obtaining isotopic information can be used like the product ion scan mode. By selecting the isotopes one by one as

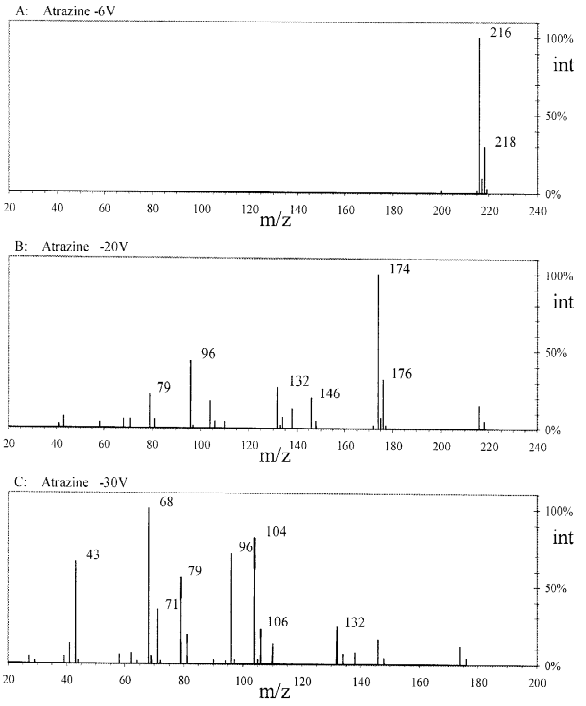

Fig. 1. Analysis of atrazine with GC–CI-MS–MS at three collision offset voltages. (A) at −6 V; (B) at −20 V; (C) at −30 V.

parent ion, specific isotope information of the product ions can be acquired. With these modes the nominal mass of the (de)protonated molecule is set at the arbitrarily value of 100% (see below).

2.2. Guidelines to add a library entry

From the spectrum, all masses can be used with intensities of over a few percent relative ion abundance in one or more of the acquired spectra (Fig. 2B). The main rule is that peaks with a relative high intensity in one or more of the acquired spectra are put in the library entry as a 100% relative intensity peak, whereas peaks with a lower relative intensity are put in the library entry as a 50% relative intensity peak. These 50 or 100% decisions are arbitrary and can be used for every collision offset voltage used during analysis. In fact, the relative intensity in the CI–CID spectrum that is produced is not important, it only serves the visual comparison of the library entry with the unknown spectrum (Fig. 2C).

The second rule is the presentation of the relative intensities of peaks representing the molecular mass

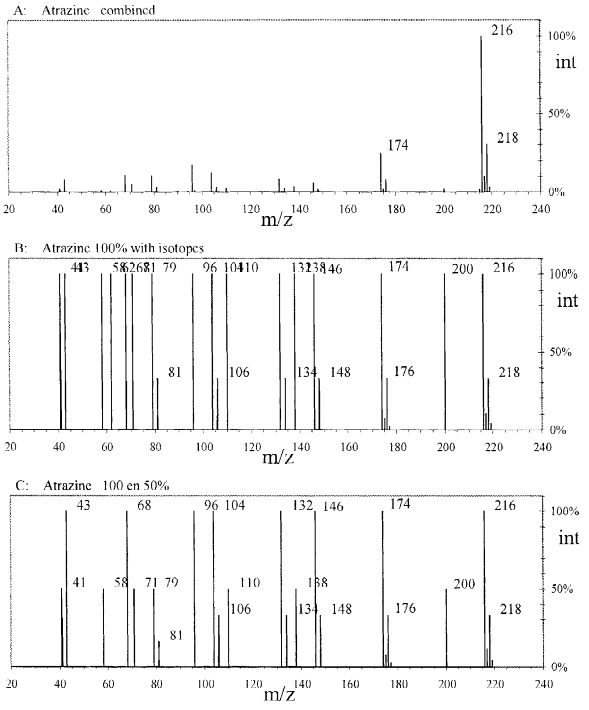

Fig. 2. Three spectra derived from the spectra of Fig. 1: (A) a combined spectrum by adding the intensities of each mass. (B) A combined spectrum showing every mass fragment ion at 100% with isotope ratios. (C) A combined spectrum showing the more intense fragments ion at 100%.

and the isotopes of the compound. With the help of an isotope pattern calculator, the theoretical intensities of the masses representing the (de)protonated molecule are put in the library entry, including the isotopic masses, i.e., the relative intensity of the molecular mass of a compound is always put as 100% despite the intensity in the actual spectrum obtained.

The third rule is the presentation of all isotopic masses of the fragment ions with known structures representing the relative high abundance (e.g., ^{37}Cl, ^{81}Br) and/or specific isotopes (e.g., ^{34}S). The relative intensities of these masses are put in as their theoretical value in the spectrum. For example, the mono chlorine isotope (^{37}Cl) of a peak with a relative intensity in the CI–CID library of 100% is put in as a 33% relative intensity peak, whereas the same mass is 16% in the case of a 50% relative intensity peak. If it is not clear whether a mass represents a fragment and/or an isotope, the m/z value is put in as a 100 or 50% relative intensity peak in the library entry.

Finally, in case of very specific adductions (e.g., the sodium adduct of oxamyl after APCI ionization [7]), the intensities of these masses are put in at 90 and 40% instead of 100 and 50%, respectively. In this way, the CI–CID library combines information and visualization.

2.3. Additional library information

In the library, several fields can be filled regarding the instrument, instrumental conditions, nominal molecular mass, CAS registry number, polarity and so on. Also, the name of the author of each library entry is available. The aim of these fields is to have more background information. Each library entry is presented in bar graph as well as in tabular graph form, whereas all other information is easily availably due to the common spreadsheet program used (Excel®).

3. Results and discussion

3.1. Masses and ratios

A mass spectrum has two types of information, i.e., masses and ratios between the masses. The EI library search algorithms use both information types to find the best fit. This is possible because EI spectra can be reproduced all over the world by using defined settings and tuning compounds. With CI however, the spectra are dependent on the conditions applied.

Fig. 1 shows spectra of the compound atrazine, acquired at three different collision offset voltages with GC–CI-MS–MS. The spectra are completely different, but represent the same compound.

Comparison of MS–MS spectra from different ionization/fragmentation systems, however, indicates, that fragment ions most often have the same masses [11,7], whereas most of the time the ratios are completely different. Therefore, we decided only to use the masses and not the ratios between the fragment ions for the CI–CID library.

Especially for large libraries it is important to have

a high specificity. More specificity is obtained by using more fragment ions, e.g., by using several collision offset voltages and specific isotopes.

3.2. Isotopes

Isotopes play an important role in the comparison of mass spectra. Especially, relatively high A+2 isotopes like ^{37}Cl, ^{81}Br, ^{34}S, etc., give specific information.

Isotopes are present in in-source fragmentation spectra, ion trap spectra with sufficient isolation width and triple quad spectra with the first mass filter at a sufficient low resolution.

As an example, the isotopic fragment ions shown in Fig. 1 were acquired with the first quadrupole at such a resolution that all isotopes of the $[M+H]^+$ ion could pass the mass filter, whereas the third quadrupole was set at nominal resolution. In the commonly used product ion or daughter ion scan mode isotopes cannot be seen, but isotopic information becomes available if, e.g., the ^{37}Cl isotope of atrazine is used as parent ion in the daughter scan mode at nominal resolution for the first quadrupole.

Compared to the isotope with the highest abundance (the A-isotope as used by McLafferty [19]) the isotopic ion ratios of a fragment ion are not influenced by the system settings applied for ionization and fragmentation, that is, the ratio is rather constant. Therefore the isotope ratios are used to create a library entry.

3.3. Library entry

Fig. 2 shows three different combined spectra derived from Fig. 1.

Fig. 2A is calculated from the spectra of Fig. 1 by adding the intensities of all ions. The result is one library entry of three different spectra with m/z ratios obtained under the conditions applied [3].

In Fig. 2B the same information of Fig. 1 is used. Now, all masses are set at 100%, except for the isotope ratios which are set at their theoretical/calculated value relative to 100%.

Atrazine has one chlorine atom, which is visible due to the presence of the ^{37}Cl isotope in several fragment ions of Fig. 1. In Fig. 2B several A+1 and A+2 isotopes are present. For the $[M+H]^+$ ion and fragment m/z 174 of atrazine the structure is supposed to be known [11], and the theoretical isotopic ratios are calculated with an isotopic pattern calculator. Some other fragment ions in Fig. 2B, of which for this example the structure is supposed to be unknown, show also isotopic masses. Isotope ratios of unknown structure fragment ions with a relative high abundance (e.g., ^{37}Cl, ^{81}Br) and/or specific isotope (e.g., ^{34}S) are set at their expected theoretical value if their presence can be derived from the acquired spectra or from specific MS–MS analyses of the isotopes of the (de)protonated molecule.

Because only the masses are used, it is not necessary to store the spectra of the different collisions energies or MS–MS stages separately. They are put together in one library entry.

3.4. Fifty and hundred % ratios

Searching the CI–CID library is based on searching for specific masses. The operator selects some of the masses of the spectrum of the unknown compound and uses a browser to search for all entries that have the same masses as the (un)known compound.

The visual comparison of the resulting library entry with the spectrum of the (un)known compound, however, is difficult because all fragment ions are shown at 100% (see Fig. 2B).

Therefore we introduced 50% intensity peaks for fragment ions that show lower intensities at all collision offset voltages applied during acquisition. This is best explained with help of Fig. 3. In this figure atrazine was analyzed at a collision offset range ramp of −6 to −56 V in steps of 5 V. Above the reconstructed ion current (RIC), traces of several fragment ions are shown. The traces reveal that the fragment ions have their maximum intensity at different collision offset voltages, but also that the maximum intensity can differ widely, e.g., the maximum intensity of m/z 110 is much lower than that of m/z 174. Based on these results we decided to divide the fragmentation ions in two levels, i.e., 50 and 100%.

Fig. 2C shows the result of the 50 and 100% decision. Compared to Fig. 2B the spectrum is easier to interpret and has many similarities compared to

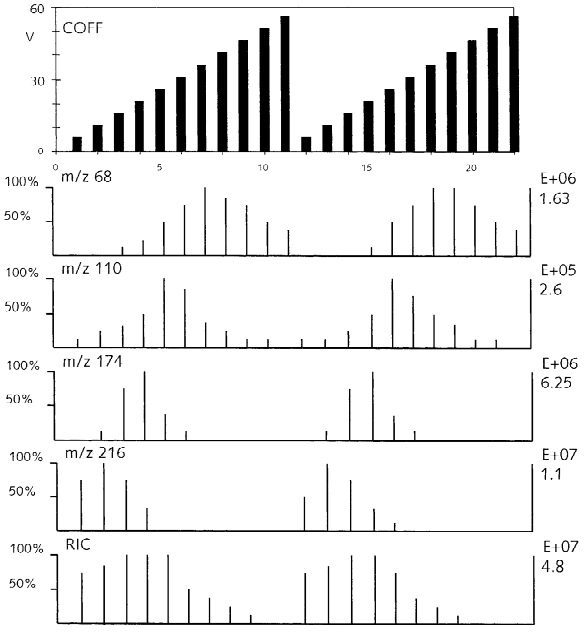

Fig. 3. FIA-APCI-MS–MS analysis of atrazine. The collision offset voltage (COFF) is ramped from −6 to −56 V in steps of 5 V. Each bar in the ion traces represents a scan.

Fig. 2A. Compared to the three figures in Fig. 1, Fig. 2C shows all high-intensity fragment ions at 100%, which is the main goal of this library, i.e., the 100% ions can be seen as the ions an operator would choose to search the library for and are normally relatively intense ions.

3.5. The CI–CID library

A spreadsheet file has been developed in Excel® to store and search the library and to add library entries. The file is available on the Internet [20]. The use of a widespread software package has the advantage that the library is independent of instrument and/or manufacturer. The choice to use an Excel® spreadsheet was made several years ago. At that time it was more difficult to interchange libraries between software packages. However, if users prefer a commercially available browser it will not be very difficult to ''translate'' the library entries to a user library.

Searching the library has to be done manually by entering some masses of the spectrum of the unknown compound into the search window of the browser

The CI–CID library contains some hundreds of entries. From these, more than 100 entries are from GC–CI-Q3 (triple quad mass spectrometer) spectra. The institute for Inland Water Management and Waste Water Treatment (RIZA) is responsible for the surface water quality of The Netherlands. A lot of compounds found in surface water are analyzed with GC–MS but can also be determined with LC–MS. Therefore we analyzed standard mixtures with a total of 400 compounds with GC–CI with ammonia-Q3 on both positive and negative ions at four different collision offset voltages in the RF-only daughter scan mode [21]. In this mode all ions are allowed to pass the first quadrupole, in contrast to the normal daughter or product ion scan mode, where only one m/z can pass the first quadrupole. At the moment, part of the spectra is entered to the library. With these entries, we and other laboratories [22] were able to identify compounds known with GC–MS but unknown with LC–MS–MS.

Some other hundreds of entries are the results of LC analyses with thermospray (TSP), APCI and electrospray ionization (ESI) and triple quad (Q3) or ion trap (trap) fragmentation. The analysis method is specified in each entry by abbreviations like, e.g., GC–CI-Q3, ESI-trap and APCI-Q3. Also, the charge is specified in a separate column and can be filtered for. To further prevent charge mistakes entries of positive ions are colored green and those of negative ions red.

The library also has 63 entries contributed by four other laboratories. Most of the contributions were the results of analysis in the daughter scan mode. Therefore, no isotopes are present in these entries. The entries based on daughter scan analyses are specified in the library to prevent wrong conclusions.

Besides the filtering of entries on the presences of the masses to be searched for, an additional search function was added to the spreadsheet file. When searching on masses, the analyst normally searches on the high abundant masses in the spectra of the unknown compound. In the entries these should be the 100% masses. By adding the percentages (100%, 50% or isotope ratio percentage) of the search masses found in each entry and sorting the totals, the

entries with the highest total percentage are shown on top.

3.6. Round robin

The CI–CID library is based on the assumption that the fragmentation pathways are the same on different mass spectrometers. To test this assumption, two mixture of 10 compounds (desmetryn, propazine, benzothiazole, metazachlor, carbamazepine, propachlor, triadimefon, diazinon, lenacil and tris(2-butoxy-ethyl) phosphate) dissolved in, respectively, dichloromethane and acetonitrile, were send to five laboratories.

The compounds are suitable to be analyzed with GC and LC and the laboratories were asked to analyze the mixture by GC–CI-MS–MS or LC–MS–MS using their settings normally used. After analysis, the spectra were sending back for evaluation.

The results are summarized in Table 1. The spectra were treated as spectra of unknown compounds and some masses were selected to search the library. In all cases the correct compound could be found easily in the library. Carefully checking the library entries with the spectra, however, revealed that especially the spectra of the triple quad systems compared very well.

Table 1
Summary of the results of the round robin test

System	Ionization	Fragmentation	Result
TSQ-7000	APCI	In-source	+
triple quad	APCI	RF-only Daughter	+
VG-Quattro	GC–CI with methane	Daughter	+
triple quad	Electrospray	Daughter	+
GCQ ion trap	GC-CI with methane	Daughter	+
LCQ ion trap	APCI	Daughter	+
Jeol HR-MS–MS	CI ammonia	Daughter	−

+: The masses in the spectra generated with the specified analysis method correspond with the masses in the library entry of the compound.
−: The spectra show several masses not available in the library entry of the compound and also not found in the contributions of the other participants.

The spectra of the ion trap systems were all analyzed in MS^2 and showed a limited number of masses comparable with spectra of the triple quad at a low collision offset voltage. Searching a large library based on these spectra might be difficult due to the lack of specific masses. In the literature, however, [11,12] ion trap spectra can be found as a result of MS^3 and MS^4 experiments. These spectra show additional masses most of the time also found in the library entry of the compound created from triple quad analyses.

The results of the HR-MS–MS measurements were a mixture of EI and CI-MS–MS masses and are therefore not suitable for library search. It is not clear whether the results are typical for HR-MS–MS or caused by specific settings applied.

4. Conclusions and perspectives

A CI–CID library for GC– and LC–MS (–MS), based on the presence of only the masses of an analyte is proposed and tested. It can be concluded, that the CI–CID library is a universal library, which can be used by operators working with chemical ionisation spectra of different ionisation techniques and different MS instruments. Because all mass information is available, users can apply their own settings to acquire the unknown compound. The usefulness is tested by applying the library in practice in our laboratory and in other laboratories. Also, entries are compared with spectra in literature and with the results of a round robin test. For GC–MS–MS analyses the CI–CID library may become a source of information additional to the large EI libraries. For LC–MS–MS analyses the CI–CID library turned out to be practical and useful.

Up to now, a lot of articles on LC–MS (MS) libraries have been published. All of them are based on a search of masses and ratios. Accepting, however, that the ratios may differ and by applying only a mass search on these ‘‘mass/mass ratio’’ libraries is already very useful. Especially, the libraries with spectra taken at different collision offset voltages have all the mass information needed. It might be stored in more then one entry, but by combining the search results the right compound can be found.

It may be expected that the number of LC–MS–

MS libraries and the number of library entries will grow in the next few years. The identification of unknown compounds is an important part of the mass spectrometric work field. For the CI–CID library only a mass search can be used. This can be done in the CI–CID library spreadsheet file, but also in the browsers of commercial libraries like the NIST and the Wiley.

The question of whether a mass search is fulfilled in a large library is best explained by the following example: the Wiley EI library has 275 000 entries. By entering a few specific fragment ions (molecular ions are generally less prominent in EI spectra than in CI spectra) for a compound and performing a mass search, an enormous reduction of the possible entries is attained. Because CI–CID spectra have more high mass ions and less low mass ions than EI spectra, it can be expected that a mass search will work better in the CI–CID library than in the EI library.

Acknowledgements

Arnold Kruize and Andre Mud are thanked for adding a lot of entries and for testing the library. Petra Scholte (WRK), Ivana Bobeldijk (KIWA), Piet Speksnijder (KIWA), Louis Maljers (Thermo-Finnigan), Joan Stäb (DZH) and Roel Fokkens (UVA) are thanked for their contribution to the round robin. Ivana Bobeldijk (KIWA), Piet Speksnijder (KIWA), Noud v.d. Borg (Thermo-Finnigan), Karel Lazou (Thermo-Finnigan), Jos Hermans (RIKZ) and Ruud van Dam (TNO-Voeding) are thanked for their contributions to the library.

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