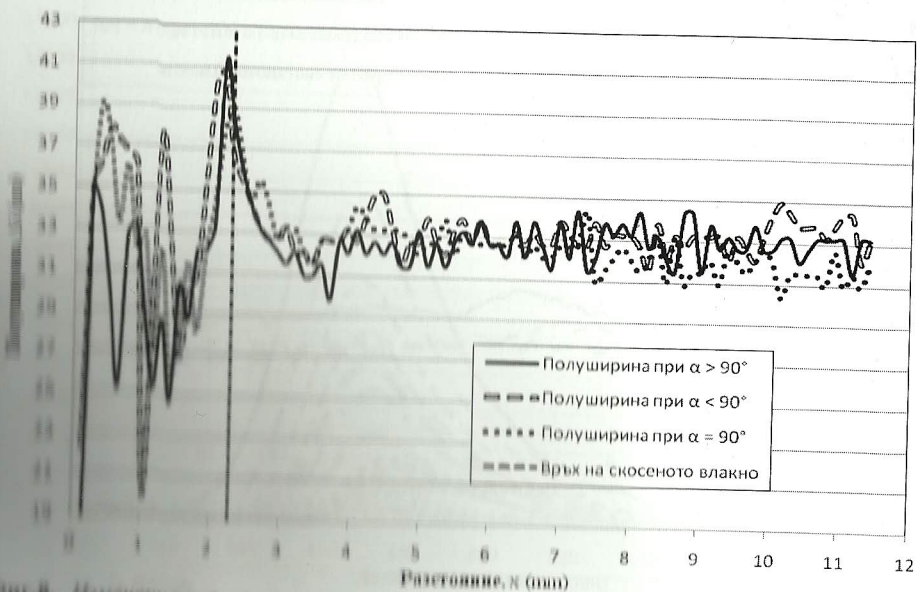


представени данни за изменението на централната дължина на вълната с максимален интензитет с промяна на възбуданата позиция за трите разгледани разположения на скосеното влакно. На Фиг. 8 са представени данни за изменението на полуширината на флуоресцентния спектър с промяна на възбуданата позиция за трите разгледани разположения на скосеното влакно.



Фиг. 8. Изменение на полуширината на спектъра на флуоресценция с изменение на позицията на възбудане.

#### Извод

Получените експериментални резултати и избраната конфигурация на възходящи едностранно-скосени оптични влакна могат да послужат за разработването на компактен компактно-оптичен флуоресцентен източник. Авторите предполагат, че би могло да се получи пренастройка на дължината на вълната на изходното флуоресцентно лъчение не само от самопоглъщане в активната среда, но и с използване на външен елемент за пренастройка. Ще бъдат проведени допълнителни изследвания с възходящи едностранно-скосени оптични влакна за установяване на поведението им при вариране на параметрите на осветяване.

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## Spectral Libraries of Vibrational Spectra

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### ABSTRACT

Several spectral databases are created that are composed of 966 absorption FT-IR, 102 ATR FT-IR and 200 Raman spectra measured in our laboratory. There are compiled four other libraries of 13484 and 350 absorption FT-IR, 12 ATR FT-IR and 116 Raman spectra from other sources. The software IRSS previously developed in our lab is used to perform spectral search in the database. The library search routines programmed in IRSS are thoroughly tested. It is found that a successful identification is possible not only of unknown compounds but of the mixtures components if their vibrational spectra are present in the vibrational spectral collections.

### INTRODUCTION

The infrared (IR) and Raman spectra reflect in a great extent the compound's structure, therefore both techniques are well suited for the process of structure elucidation [1,2]. Though Raman spectroscopy has only recently been introduced for analytical purposes, it was applied since the middle of the previous century as a vibrational technique that provides spectral information complementary to middle IR (MIR) spectroscopy. Similar to the MIR spectrum, the Raman spectrum is based on molecule fundamental vibrations and their overtones thus providing a detailed spectral "fingerprint" of the compound under study. As an analytical technique, Raman spectroscopy offers many advantages over MIR spectroscopy [2,3]; the most important of them are the following: (1) little or no sample preparation is required; (2) water as a liquid is a weak scatterer - no special accessories are needed for measuring aqueous solutions; (3) water vapors and carbon dioxide are very weak scatterers - sample compartment purging is unnecessary; (4) fiber optics (up to tens of meters in length) can be used for remote analyses; (5) Raman bands are narrower and both the overtones and combination bands are generally weak; (6) the spectral range reaches well below  $400\text{ cm}^{-1}$ , making the technique applicable to organic compounds containing heavier elements; (7) The symmetric molecular vibrations which appear as low-intensity bands in the IR spectrum exhibit very strong Raman bands.

Attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy is one of the more popular sampling techniques used by FT-IR spectroscopists because the measurement is quick, non-destructive and requires virtually no sample preparation [2]. An ATR spectrum is slightly different from an MIR one of the same compound measured in KBr pellet or as a thin layer: ATR spectral bands are narrower and band relative intensities are also different from those of the absorption IR spectrum. That poses a challenge when IR spectra are searched in ATR library and vice-versa.

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Library search systems for MIR and Raman spectra and the corresponding spectral libraries are currently commercially available from both the instrument manufacturers and chemical software businesses together with search and retrieval software [4,5]. Also, vibrational spectral libraries consisting of several hundreds to thousands of spectra can easily be produced on a computerized instrument. Despite that, the number of commercially available and lab-produced spectra is way smaller than the number of currently known compounds (around 75 millions). That is why, the composition of new spectral collections is of a great importance for analytical chemistry.

This paper reports on a preparation of databases of FT-MIR, ATR FT-MIR and Raman spectra. Some of the spectra are measured in our lab but there are spectra taken from other sources. A library search in Raman spectral databases is thoroughly tested with spectra of individual organic compounds and their mixtures.

## METHODS

The library search consists of comparison of a spectrum of the unknown with a collection of reference spectra of compounds with known structure [1,4-6]. The collection of spectra together with both chemical information and structure of the compounds is called a spectral library. The result obtained by a search, the so-called *hitlist*, is a list of spectra (hits) that are most similar to the query spectrum. The hits are sorted in the hitlist according to a real number referred to as *hit quality index* (HQI) which reflects the similarity between the unknown and reference spectrum. If the unknown is among the library entries, then the correct answer often appears among the first several hits and a visual inspection of them makes it possible to identify the unknown: this is called *identity search* [6]. However, if the unknown compound is not among the library spectra, a more sophisticated interpretation of the hitlist is necessary [7]. Assuming that similar spectra indicate similar structures, the hitlist structures characterize the unknown structure: this is the essence of the *similarity search* [6].

For both types of searches important aspects are the representation of the spectra, the spectral similarity measures used and the search algorithm applied [1]; for the similarity search another key characteristic is the method of analysis of the hitlist structures. Other characteristics of a library search system include the speed and versatility of the implemented search algorithms, the size, contents and reliability of the database, the options for an update of spectral library, the availability of modules for analysis of the hitlist entries and the possibility to derive spectrum-structure correlations.

## EXPERIMENTAL

The method for library search is implemented into a Windows-based user-friendly program, called IRSS [7,8]. Seven different algorithms for the comparison of IR spectra are implemented: three methods for peak matching [8,9] and four methods for comparing full spectral curves [7]. Furthermore, IRSS contains software tools for an import of IR spectra in JCAMP-DX format, peak picking, and an interactive analysis of IR spectra of mixtures based on multiple linear regression techniques.

Some of the MIR spectra (see Table 1) are registered on a Perkin-Elmer 1750 FT-IR Spectrometer from 4000  $\text{cm}^{-1}$  to 450  $\text{cm}^{-1}$  at resolution 4  $\text{cm}^{-1}$  with 25 scans. All these spectra are subjected to curvilinear baseline correction and off-line converted into JCAMP-DX files. The latter are transferred to an IBM compatible computer with the standard protocol for data exchange KERMIT. The new MIR spectra (see Table 1) are measured on a VERTEX 70 FT-IR spectrometer (Bruker Optics) from 4000  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$  at resolution 2  $\text{cm}^{-1}$  with 25 scans. For all MIR spectra the solid samples are prepared as KBr pellets and liquids are measured as a capillary film between KBr plates.

The ATR FT-IR spectra are recorded with a VERTEX 70 FT-IR spectrometer; the spectrum is measured from 4500  $\text{cm}^{-1}$  to 600  $\text{cm}^{-1}$  at resolution 2  $\text{cm}^{-1}$  with 16 scans. The used ATR accessory is MIRacle™ with a one-reflection ZnSe element (Pike). For solid samples the stirred crystals of

compound are pressed by an anvil to the reflection element; for liquid samples a drop is placed directly upon the crystal plate of the accessory.

The FT-Raman spectra are measured on Bruker Optics RAM II module coupled to a Vertex 70 FT-IR instrument with a focused laser beam of Nd:YAG laser (1064 nm) from 4000  $\text{cm}^{-1}$  to 51  $\text{cm}^{-1}$  at resolution 2  $\text{cm}^{-1}$  with 25 scans: the laser power varies from sample to sample from 10 mW to 1000 mW. The solids are placed as stirred crystals in aluminium disc and liquid samples are recorded in standard NMR tubes.

A very large-size spectral library of 13 484 spectra, CC (Chemical Concepts), has been created earlier from the MIR spectra of SpecInfo database [7]; its composition is described there in detail.

Two libraries, an ATR and a Raman one, are composed from spectra measured in Julius Kühn-Institute, Berlin; these spectra are used with the kind permission of Dr. Gennady Gudy. The ATR FT-MIR spectra have been recorded in the wavenumber range from 4000 to 375  $\text{cm}^{-1}$  with a portable ATR diamond crystal infrared spectrometer (Alpha, Bruker Optics GmbH, Ettlingen, Germany). The corresponding FT-Raman spectra are recorded on an RFS-100 Bruker FT-spectrometer.

The Bruker Demo FT-IR library of 350 entries (which is delivered with the OPUS software) have been converted into our spectral format.

For test purposes additional Raman spectra of (a) 20 individual compounds (see Table 2a), (b) two types of binary mixtures prepared with varying volume fraction (see Table 3), and (c) three individual compounds available as small crystals are measured (see Table 2b). The Raman spectra in (a) and (b) lists are measured on RAM II module as described above but the three tiny crystal samples are measured on RamanScope II microscope (with Nikon objective  $\times 10$ ) coupled to RAM II module of the Vertex 70 FT-IR instrument.

All spectra except those registered on the old Perkin-Elmer instrument have been available on PC computer as ASCII files in JCAMP-DX format, v. 4.24. The spectra in JCAMP files are converted into our spectral format.

The structures are prepared with ISISDraw, v. 2.4 (MDL, Inc.); MOL files are exported by this software and read by IRSS to create the chemical structure files. The IRSS software and all spectral libraries created with our spectra are available from the corresponding author.

**Table 1.** The compiled spectral libraries.

a) with spectra measured in our laboratory			
Lib. Name	Spec. Type	Num. of Spectra <sup>1</sup>	Instrument <sup>2</sup>
IR01	MIR	105 / 105	PE
IR02	MIR	181 / 161	PE, Br
IR03	MIR	197 / 144	PE
IR04	MIR	179 / 179	PE
IR05	MIR	52	PE, Br
IR06	MIR	197	PE
IRSub	MIR	55 / 37	PE, Br
ATR	MIR	102	Br
Raman	Raman	200	RamII

<sup>1</sup> The second entry is the number of old spectra.

b) with spectra from other sources

Lib. Name	Spec. Type	Num. of Spectra	Instrument <sup>3</sup>
CC <sup>3</sup>	MIR	13 484	unknown
Bruker	MIR	350	PE
ATRp	MIR	12	Alpha
RamP	Raman	116	RFS

<sup>2</sup> PE = Perkin-Elmer 1750 FT-IR Spectrometer; Br = Bruker FT-IR Vertex 70 Spectrometer; RamII = Bruker Optics RAM II module; Alpha = portable ATR diamond crystal infrared spectrometer; RFS = RFS-100 Bruker FT-spectrometer.

<sup>3</sup> Chemical Concepts, SpecInfo MIR database.

## RESULTS AND DISCUSSION

In years 1992-98 three FT-IR libraries of 608 spectra have been created [10]. In 2011-12 with the support of the Bulgarian National Science Fund, Contract DDWU02/37, these databases have



been expanded with other nearly 500 FT-IR spectra and an FT-Raman library of 200 entries is also created. For the project NI13ChF006 (University of Plovdiv) an ATR FT-IR library of 102 spectra is composed [11]. All three types of spectral databases are maintained by the IRSS software that has been created for absorption FT-IR spectra. That is why, it is necessary to test the library search routines with Raman and ATR spectra; the IRSS software is thoroughly tested for absorption FT-IR spectra [9-10]. The comprehensive test of the performance for search of ATR FT-IR spectra (as unknowns) in absorption FT-IR spectral libraries and vice versa has been reported earlier [11]; here only the performance of the library search of Raman spectra in an FT-Raman database is described.

**Table 2.** The test spectra. The laser power of the corresponding reference spectra (Lib) and test spectrum (Unk) is given.

a) measured on Bruker Optics RAM II module.

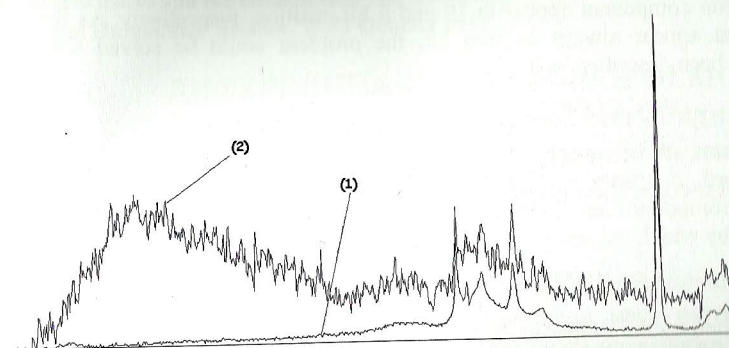
#	Compound	Laser power / mW	
		Lib	Unk
1.	1,4-Dioxane	700	500
2.	2,2,4-Trimethylpentane	500	100
3.	Dichloromethane	500	100
4.	3-Methyl-1-butanol	500	100
5.	n-Butyl acetate	500	50
6.	1-Decanol	700	100
7.	Dodecane	500	100
8.	Phenyl-acetonitrile	200	20
9.	Acetic acid linalylester	200	50
10.	Squalene	500	100
11.	1-Hydroxy-3-nitrobenzene	100	20
12.	1-Hydroxy-4-nitrobenzene	200	10
13.	3-Nitro-benzamide	500	100
14.	Diethyl ether	700	100
15.	Carbon disulfide	400	100
16.	Carbon tetrachloride	1000	100
17.	Acetonitrile	500	100
18.	Dimethyl sulfoxide	1000	100
19.	1-Nitro-3-trifluoromethyl-benzene	500	100
20.	Tetracyanoethylene	100	50

b) measured on RamanScope (Bruker), x10.

#	Compound	Laser power / mW	
		Lib	Unk
1.	Oxalic acid	200	700
2.	2-(2,2,2-Trichloro-acetylamino)-benzamide	200	500
3.	L-Histidin-methylester-dihydrochloride	500	500

As the absolute band intensity in the FT-Raman spectrum is dependent on the laser power, the Raman spectra vary nearly linear with the change of the latter [3]. As the higher laser power means higher signal to noise (S/N) ratio, the Raman spectra are preferably measured at highest laser power that does not decompose the sample (the so-called *burning* is observed only for solid samples). When we measured the library spectra we could allow ourselves to increase the power up to the burning level and use the last good spectrum as a library one. That is why, the library spectra are measured at very high laser power and are with the best-possible S/N ratio. But when the spectroscopist measures a sample of an unknown organic compound he/she try to preserve it

intact; usually the sample is recovered back from the disk – otherwise the advantage of Raman spectroscopy as non-destructive technique is lost. As a result, the Raman spectrum of an unknown is usually measured at a laser power lower than that of the library spectrum.



**Figure 1.** Raman spectra of oxalic acid: (1) measured on Ram II in aluminium disk, (2) registered on Raman microscope, x10.

Of course, library and unknown spectra are scaled in 0.0 - 1.0 range in ordinate but a different band intensity means also a different band width and sometimes two bands with peaks, close in wave number, merge at higher laser power into one. That is why, it is necessary to test the search algorithms with spectra of the library compounds that are measured at different laser power. This is done with the Raman spectra of 20 library compounds from Table 2a. All of them appear as first hit when searched in the library of 200 Raman spectra. The three spectra from Table 2b, measured on Raman microscope at laser power higher than that of the corresponding reference, are searched in the same library. Two of them are ranked as first hit, the other, oxalic acid, as second hit. (Here has to be mentioned that the microscope Raman spectra are usually measured at higher power because of their low S/N ratio; the latter could be seen from spectra in Figure 1.)

**Table 3.** Backward peak search results: hit position of the mixture components. Search tolerances are  $\Delta A = 11 \text{ cm}^{-1}$  and  $\Delta v = 1.0 \text{ a.u.}$

a) mixtures of butyrophenone and valerophenone.

#	Mixture composition v/v <sup>1)</sup>	Butyrophenone	Valerophenone
1.	4:1	1	2
2.	3:2	1	2
3.	1:1	2	1
4.	2:3	2	1
5.	1:4	2	1

b) mixtures of cyclopentanone and benzylacetone.

#	Mixture composition v/v <sup>1)</sup>	Cyclopentanone	Benzylacetone
1.	4:1	1	10
2.	3:2	1	3
3.	1:1	1	2
4.	2:3	1	2
5.	1:4	0	1

<sup>1)</sup> volume ratio



The Raman spectra of two series of binary mixtures are measured; their composition and the hit position of both components are given in Table 3. The components in the first series can be successfully identified but the 4:1 v/v and 1:4 v/v mixtures from the second series give worse results – the low-concentration component appear in 10 and 9 hit position, respectively. As the high-concentration component appear always as first hit, the problem could be solved with spectrum subtraction as it has been described in [9].

### CONCLUSIONS

The created spectral libraries are of significant help in compound identification if the query compound has a library record. A search in Raman spectral library is thoroughly tested with spectra of individual organic compounds and their mixtures. Similarly to MIR spectra, the Raman spectra provides a fingerprint by which the compound or mixture component can be identified.

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## ДИФЕРЕНЦИАЛЕН ТЕГЛОВЕН ОСМОМЕТЪР Кирил Коликов<sup>1</sup>, Димо Христов<sup>2</sup>, Радка Колева<sup>1</sup>

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### Резюме

В представената работа ние описваме трикамерен диференциален тегловен осмометър. Преминалата през две полупропускливи мембрани маса разтворител в разтвора се определя с помощта на електронна везна. Измерената маса служи за директно сравняване пропускливостта на различни мембрани към един и същ вид разтвори. Сравняват се и осмотични потоци на разтворител към два различни разтвора – като вид и/или концентрации. Чрез предаване на отчитаните от електронната везна стойности към компютър с подходящ софтуер директно се определя и се изписва графично разликата от плътностите на осмотичните потоци.

**Ключови думи:** осмоза, мембрани, осмометри, плътност на осмотичния поток.

### 1. Въведение

Осмозата е едностранна дифузия на разтворител към разтвор, които са разделени чрез полупропусклива преграда – мембрана. Намалването масата, т.е. обема, на разтворителя и увеличаването масата, т.е. обема, на разтвора с течение на времето е характерна особеност на процеса осмоза. В даден момент време се получава равновесно състояние – в разтвора повече не преминава разтворител, поради изравняване на наляганията от двете страни на мембраната. В това състояние по манометричния метод разликата между хидростатичните налягания на разтвора и на разтворителя е измереното осмотично налягане [1].

В [2] е описан тегловен осмометър, в който съдът с разтвора е окачен на едното рамо на лостова везна и е потопен в разтворителя. Недостатък на този осмометър е, че има изпарение на разтворителя, който е отворен към атмосферата. Друг недостатък е, че осмозата е бавен процес, а атмосферното налягане се изменя с времето.

За първи път в [3] са предложени везнови (тегловен) метод и устройство за изследване на дифузията в течни прозрачни и непрозрачни среди. Развита теория е пример за задълбочен подход към труден проблем, но описаното експериментално устройство е сложно и трудно реализуемо.

В [4] и [5] са описани тегловни осмометри, чрез които осмотичният процес се изследва с везна. Тези изследвания, обаче, се извършват за всяка мембрана чрез отделен експеримент. Така окачествяването на мембраните изисква много време и измерването не е достатъчно точно, поради промяна на началните условия при различните експерименти.

В настоящата работа даваме по-нататъшно развитие на тези осмометри. С описаният тук трикамерен диференциален тегловен осмометър, се измерват два осмотични потока през различни мембрани, които се сравняват във всеки момент време.

### 2. Трикамерен тегловен осмометър

На **Фиг. 1** схематично е изобразено вертикално осево сечение на предлагания от нас трикамерен диференциален тегловен осмометър, състоящ се от корпус *C*, плът *B* и