FTIR spectrometry is particularly well suited to the identification of compounds in all kinds of aggregation states. A classic infrared spectrometric analysis is that of solids, which are embedded in potassium bromide (KBr) and pressed into pellets. Another application area is the measurement of solvents that are preferably water-free, using cells.

Water has always been considered to interfere with infrared measurements and was removed via suitable methods, for instance drying. Water with its –OH vibrational bands generates a strong, completely overlapping spectrum (Figure 1).

The purpose of this application is to demonstrate that not only water with its –OH group can be analysed, but also ‘light’ isotopically labelled water with its –OD groups. The analysis is not limited to the identification of the molecular vibrations but also attempts the quantitative determination in simple matrices such as water and even in complex matrices such as body fluids.

Sensitivity, accurate and fast – the FTIR technique

In addition to high sensitivity, accuracy and reproducibility, FTIR also offers another important analytical criterion: speed of analysis. We will show that fast FTIR measurement generates results that are comparable with the more complex and time-consuming mass spectrometric determinations commonly used for these types of analyses.

To illustrate the features of the two types of analysis, very different application areas are selected. In natural water – in this study the Russian rivers Neva – the percentage of deuterated water is of interest from an ecological point of view. In the analysis of body fluids, deuterated water is often used to study metabolic processes. One such application is the study of the exchange of substances between mother and child during breastfeeding. A control group of ten mothers were given a known concentration of deuterated water to drink. After a certain period of time, samples of breast milk and saliva were collected from mother and child. These samples were analysed via FTIR.

Theory

The effect of substitution with deuterium against hydrogen atoms causes a shift in valence vibrational bands. The literature reports the vibrational bands $v_{OD}$ at 3643 and $v_{OD}$ at 2651 cm$^{-1}$ in the gas phase, and the method of calculation. Considering the literature data and looking at the bands at approximately 3300 cm$^{-1}$, which corresponds to the –OH vibration of the liquid aggregational state of water, the position of the corresponding –OD vibration is calculated to be approximately 2440 cm$^{-1}$. Figure 2 shows the theoretical positions of the valence vibrational bands.

In practice, both applications discussed here show a wavenumber range of 2600 to 2400 cm$^{-1}$ for the –OD vibrations (Figure 3). When the deuterium concentration in water is low, only the HDO molecule is formed because the equilibrium is shifted towards the right-hand side of the equation: $H_2O + D_2O \leftrightarrow 2HDO$; $K = 4.2 \times 10^{-3}$.

From the above, it is concluded that the concentrations are interrelated as follows: $C_{H2O} = \frac{C}{C_{H2O} + C_{D2O}}$ i.e. the concentration $C_{H2O}$ is proportional to $D$. In addition, during the analysis one has to take into account that water exhibits a high absorption band in this range and that even the CO$_2$ doublet signal can interfere with the determination. This imposes extra requirements on the measuring technique and the detection method.

Accessories

Classical measuring cells with water-resistant CaF$_2$ windows are used in both applications. In the case of natural water, cells with pathlengths of 0.1 mm and 0.2 mm are used and a 0.2 mm pathlength was used for the –OD determination within the range of the detection limits. The measurements were carried out on Shimadzu FTIR-4200 series instruments.

Sample preparation

Saliva and breast milk samples were centrifuged and the samples were subsequently transferred to the IR measuring cell. After IR measurement, the samples were analysed via MS. The natural water samples were transferred directly into the cells. These minimal sample preparation steps are sufficient to meet the requirements for fast and relatively interference-free sample preparation and measuring techniques.

Evaluation of the measuring results

The analysis of deuterated water is based on the accuracy provided via FTIR techniques and consequently the accuracy in the difference between absorption of a sample with respect to a standard. Water with a known percentage of deuteration is used. Water with higher or lower deuteration can be determined against a known reference. In the case of natural water analysis, the standard was a water sample spiked with D$_2$O at a deuterium content of 0.2018%, which had been determined via comparison measurement using MS. The sample was unlabeled water from natural origin that usually exhibits a deuterium content of 0.214 – 0.216%. In order to confirm these values, water from the river Neva was used for analysis.

For representation of the –OD bands, the ‘light’ water spectrum of the standard (Figure 5) was subtracted from the Neva riverwater spectrum (Figure 4). The result is shown in figure 6 with the maximum of the –OD bands at approximately 2500 cm$^{-1}$. The analysis of the sample shows a shift of 0.016 % deuterium. The MS analysis results in a value of 0.014 % deuterium.

In the case of body fluids, the interpretation of the spectra was carried out in the same way. Standard spectra were acquired and these were subtracted from the sample spectra. The standard spectra were generated through addition of D$_2$O to water. The analysis was carried out as a time-dependent experiment. Therefore a reference spectrum was obtained for the body fluids at a time t = 0, without the influence of the deuterated water. The results of the body water kinetics, when comparing IR with MS analyses, are shown in the following table. These Ferm values, in relation to the total composition of breast milk consisting of approximately 87 % water, result in a calculated volume of 852 ml.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water from mother to child (Fmm)</th>
<th>M = Fmm/0.87 (ml/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Breast milk</td>
<td>0.78</td>
<td>0.10 MS</td>
</tr>
<tr>
<td>Breast milk</td>
<td>0.74</td>
<td>0.10 FTIR</td>
</tr>
</tbody>
</table>

Table 1: Results after acquisition and evaluation of the deuterated samples. Where Fmm represents the average continuous travel of water from mother to infant. M is the conversion factor for the total volume of breast milk exchanged. MS = mass spectrometry, FTIR = Fourier transform infrared spectrometry

Conclusions

The high sensitivity of this method is based on high baseline stability, high signal-to-noise ratio and data accuracy of the photometric method. For the natural water sample, a detection limit of 0.003 % deuteration could be obtained. Furthermore, FTIR was proven to be a fast technique, as only 12 minutes were needed from sample preparation to data evaluation. For body fluids, representing a more complex sample matrix, concentrations less than 200 ppm could be detected via FTIR. FTIR measurements with respect to water kinetics are all comparable with the reference MS method.

References

* Yu. Predtechenskii and N. Kholodova, “Rapid Determination of Deuterium Content of Water by FTIR-HDO”, Russian Scientific Center Applied Chemistry, St. Petersburg, Russia


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FIGURE 1: IR spectrum of water (L = 0.02 mm), where L = pathlength of the cell

FIGURE 2: Representation of the theoretical position of the –OH (red) and –OD (blue) valence vibrational bands in an infrared spectrum

FIGURE 3: Spectrum of deuterium-labelled water 1 % D$_2$O (L = 0.1 mm), $v_{HDO} = 2500$ cm$^{-1}$

FIGURE 4: Spectrum of Neva riverwater (L = 0.2 mm)

FIGURE 5: Spectrum of deuterated water with deuterium concentration of 0.0018 % (L = 0.2 mm)

FIGURE 6: Difference spectrum of Neva riverwater and deuterated water

FIGURE 7: Difference spectrum of Neva riverwater and deuterated water

Subtracted Data: NEVA02.IRS - 1 * LIGHT02.IRS

FIGURE 8: Spectrum of Neva riverwater with deuterium concentration of 0.0018 % (L = 0.2 mm)

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Deuterium in Body Water using an FTIR

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Deuterium in Body Water using an FTIR

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**Fast determination of deuterated water in body fluids and natural waters**

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**Theory**

The effect of substitution with deuterium against hydrogen atoms causes a shift in valence vibrational bands. The literature reports the vibrational bands of $v_{\text{OD}} = 3843$ and $v_{\text{OD}} = 2615$ cm$^{-1}$ in the gas phase, and the method of calculation. Considering $\delta$ the literature data and looking at the bands at approximately 3300 cm$^{-1}$, which corresponds to the –OH vibration of the liquid aggregational state of water, the position of the corresponding –OD vibration is calculated to be approximately 2842 cm$^{-1}$. Figure 2 shows the theoretical positions of the valence vibrational bands.

In practice, both applications discussed here show a wavenumber range of 2600 to 2400 cm$^{-1}$ for the –OD vibrations (Figure 3). When the deuterium concentration in water is low, only the HDO molecule is formed because the equilibrium is shifted towards the right-hand side of the equation: $H_2O + D_2O \rightarrow 2HDO_{(l)} = 4.0 (300 °K)$.

From the above, it is concluded that the concentrations are interrelated as follows: $C_{\text{HDO}} = 1-C_{\text{DHO}}$, i.e. the concentration $C_{\text{HDO}}$ is proportional to $D$. In addition, during the analysis one has to take into account that water exhibits a high absorption band in this range and that even the CO$_2$ doublet signal can interfere with the determination. This imposes extra requirements on the measurement technique and the detection method.

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*Yu. Predtechenskii and N. Kholodova, Rapid Determination of Deuterium Content of Water by FTIR-8400, Russian Scientific Center Applied Chemistry, St. Petersburg, Russia


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