Trouble Shooting Information

Analysis with Merck · All you really need

Potassium bromide for Infrared spectroscopy UVASOL®

Infrared spectroscopy today

Infrared spectroscopy is one of the oldest analytical techniques[1] used today. Its versatility of use for numerous analytical problems and a great variety of sample types reflects its value as an analytical tool. Within the medium range (400-4000 cm^{-1}), it can be used for the following applications:

- Structural analysis of organic and inorganic compounds
- Identity and polymorphic testing (e.g. of pharmaceutical active ingredients)
- Quantitative determination of environmental contaminants (e.g. hydrocarbons in drinking water, gas pollution analysis)
- Micro-analytical procedures using the infrared microscope
- Monitoring reactions and kinetics (time-based and in-situ IR spectroscopy).

In addition, near-infrared spectroscopy within the range 4000-12000 cm^{-1} is developing into one of the most important analytical techniques[2] in in-process control, whether as a hydrocarbon sensor in waste water control or in the on-line control of blenders in pharmaceutical manufacturing.

This development is based on revolutionary instrument technology, the conventional grating being replaced by computer-controlled Fourier-transform spectrometers[3]. These are substantially more sensitive and fast in terms of measuring speed. Analytical determinations in micro- and trace analysis are routine today[5].

Sample preparation

In contrast to the changes that have taken place in instrument technology, sample preparation in IR spectroscopy has remained practically unaltered. The technique of potassium bromide pelletising[4] e.g. has survived from the 1960s as the standard method for measuring transmittance of solids. The quality specifications established for potussium bromide in 1963 were[7]:

1. It should show no inherent contamination absorption bands
2. When grinded with the substance to be investigated, it should produce a completely homogeneous and, in the ideal case, transparent pellet
3. These requirements should be able to be fulfilled whilst the potassium bromide remains easy to handle

In view of the high performance of today's IR instruments, these requirements have to be re-defined. Apart from the quality demanded of the embedding material itself, its handling during preparation should be viewed critically, especially as this has some considerable effect on the overall workload involved in the analytical laboratory. However, the quality of the potassium bromide should fulfill all relevant requirements.

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A new specification for potassium bromide

The quality requirements cited above cannot be fulfilled in all respects, principally due to the strong hygroscopic nature of potassium bromide; the finer the particle size of KBr, the more transparent the pellet but the more rapid is its contamination by water[7]. During storage, the material becomes cake-like in its consistency, especially if it comes into contact with the moisture of the air. In addition, KBr tends to absorb volatile organic compounds from the surrounding air. UVASOL®, prepared by a special method of purification and subsequent treatment, is adjusted to a mean particle size of 150 µm.

This is sufficient for the preparation of perfectly good pellets without the need for further pre-treatment and the associated risk of contamination. It also retains its powdery form over a period of years if stored in an air-tight condition.

Its physical suitability for pelletising is checked by a special application test and its chemical purity established by full spectrum FT-IR analysis. The intensities for the OH- and CH-bands in particular are indicated as these occur frequently in critical applications (see fig. 1).

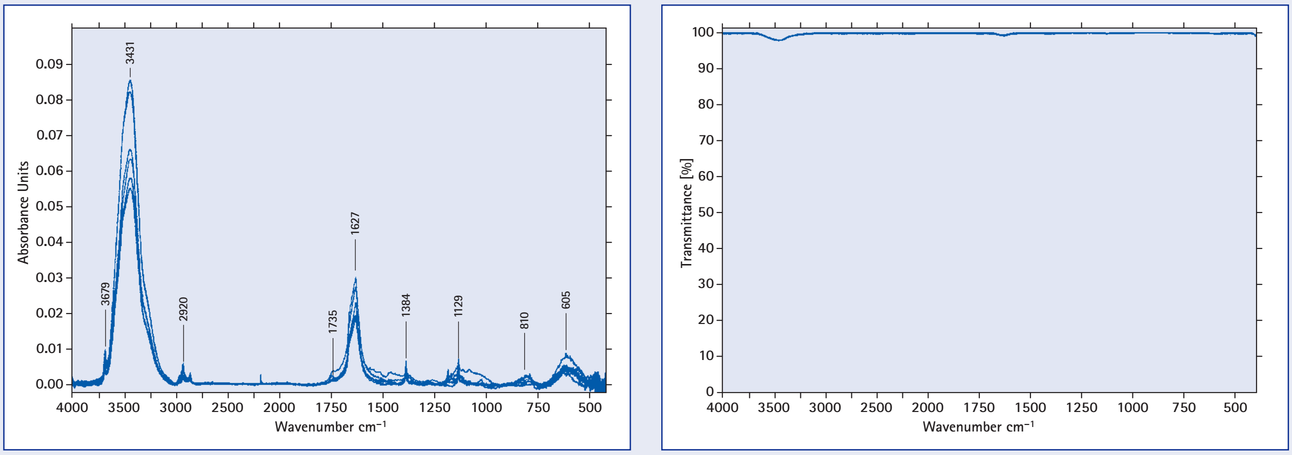

Fig. 1: FT-IR absorbance spectra of representative batches of Uvasol® potassium bromide at 5 mm path length and transmittance spectra (blank) at 0.7 mm path length (32 scans, 2 cm^{-1} resolution, DTGS detektor, Bruker IFS-48)

Application testing

Press 2 g of KBr directly in a 13 mm pressing tool for 15 min under 10 t/cm^2 pressure and 20 mbar vacuum. The resulting pellet must be compact and transparent.

Place the pellet directly in the standard sample mount of a FT-IR spectrometer that has been flushed with highly pure and dried nitrogen. Measure at 2 cm^{-1} resolution. Compare the spectrum generated with that of an empty sample chamber (N_2-atmosphere). The following requirements must be fulfilled:

Absorbance (5 mm path length):

Water	max. 0.15	within range 3250-3750 cm^{-1} and 1620-1640 cm^{-1}
Hydrocarbons	max. 0.004	within range 2750-3100 cm^{-1}
Other (e.g. NO_3^-, SO_4^{2-}, SiO_2)	max. 0.015	within range 420-4000 cm^{-1}

The normal path length used in routine analysis with the pellet is 0.7 mm (ca. 300 mg KBr). For this path length, the guaranteed transmittance is 95% for H_2O (3250-3750 cm^{-1}) and 99,9% for hydrocarbons (2750-3100 cm^{-1})

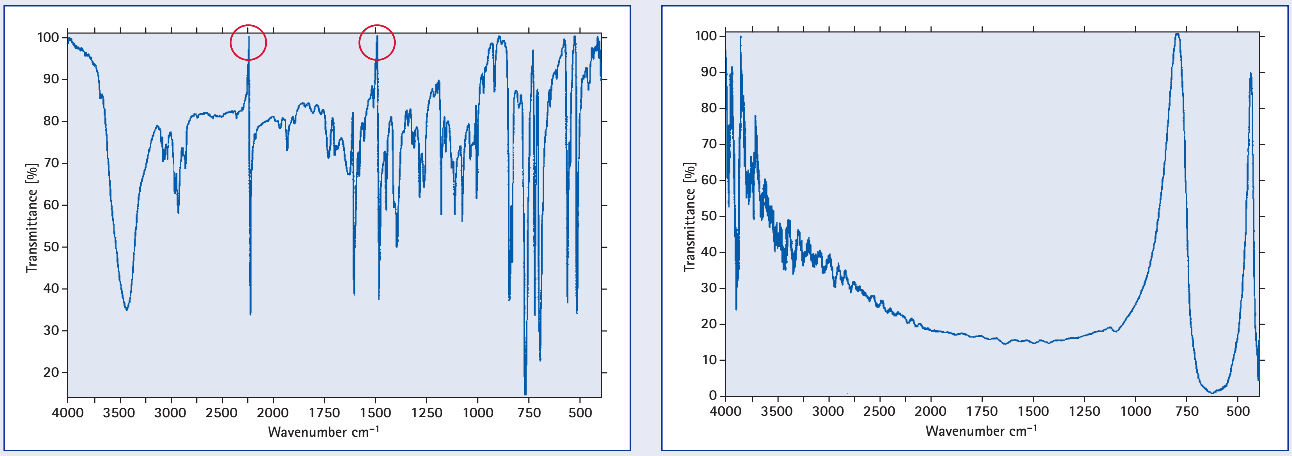

Fig. 2: Interference caused by the Christiansen effect in combination with automatic baseline correction (rubber band method) in FT-IR transmittance spectra of an organic substance and an inorganic oxide in KBr (1 mg sample/300 mg KBr)

Problems that can occur in routine work

The application limits for KBr pellets are given in standard works on IR spectroscopy[1,6,8].
For convenience, they are summarised in the table below.

KBr pelletising	Influence on the sample	Spectral error with	Remedy or alternative action
Pressure	Decomposition, Structural change, Phase conversion	Polymorphic analysis, Identity analysis of labile substances	Use liquid embedding agents like paraffin (UVASOL® Cat. No. 1.07161) and compare the spectra; diffuse reflection spectroscopy (DRIFT) of KBr (UVASOL® Cat. No. 1.04907) substance powder mixture.
Hygroscopy of KBr	Dehydration	Analysis of hydrates and solvents	Liquid embedding agents
H_2O and O_2 content in KBr; contact with air	Reactions within pellet	Strongly hygroscopic, hydrolysable and oxidation-sensitive samples	Preparation under inert gas, pellet in sandwich technique: carefully coat and pelletise pure KBr/KBr+ sample/pure KBr
Ionisity of KBr	Ion exchange	Organic salts in particular	Liquid embedding agents
Reactivity of bromide	Reduction, brown colouring (Br_2)	Strong oxidising agents	KCl or liquid embedding agents
Density of KBr too low	Distribution not uniform as substance precipitates within pellet	Substances of high density (e.g. lead compounds)	Reduce particle size substantially in a vibratory mill; diffuse reflection (DRIFT)
Refractive index of KBr too low	Turbid pellet due to Christiansen effect	Substances with too high and/or too large particle size	Reduce particle size by milling with KBr and/or use other embedding agent (e.g. KI, Cat. No. 1.05044)

Mistakes are avoidable

Apart from the above-mentioned basic limitations of the KBr pelletising technique, avoidable problems can arise as a result of improper handling of the KBr itself as well as when measuring with FT-IR spectrometers and carrying out software-assisted spectral manipulation.

Problem	Cause	Remedy
Pellet shows intensive CH-bands (3200-2600 cm^{-1})	Contamination with organic vapours or organic substances (mortar used for paraffin and KBr, same spatula for KBr and sample, handcream still fresh, gloves ...)	Store KBr in a clean and closed off atmosphere and only open for removal, separate spatula for KBr, separate mortar for KBr, no plastic equipment
Pellet shows intensive H_2O-bands (3600-3400 cm^{-1})	KBr in contact with moisture, improper storage, measurement in FT-IR instrument without sample flushing; the press is not dry or apply a vacuum using a water jet pump	Dry the KBr by heating under vacuum at 300 °C, store KBr, mortar and equipments in dry oven at 50 °C, use instrument with sample compartment flushing facility, shorten sample preparation time, measure pellet directly
Spectrum exhibits sharp, in some cases even negative bands at 3600, 2000 and 1600 cm^{-1}	Inclusion of air bubbles in pellets insufficient cleansing of the sample chamber over or under compensation by the air reference spectrum	Evacuation of the press during pellet manufacture, increase duration of cleansing cycle; record reference spectrum before each and every determination; check 100 % line
High noise level >1000 cm^{-1}, steep "negative bands", irregular baseline (see fig 2)	Christiansen effect brought about by turbid pellet due to too large particle size or too high refractive index of sample in combination with automatic baseline correction. Transmittance decreases rapidly towards higher wave numbers, ultimately achieving total absorption. The automatic baseline correction facility creates distorted spectra.	Mill the sample, switch off automatic baseline correction

References

[1] B. Schrader (Ed.), Infrared and Raman Spectroscopy, VCH Verlagsgesellschaft, Weinheim (1995).
[2] W. F. McClure, Near-Infrared: The Giant is Running Strong, Anal. Chem. 66 (1994) 43A.
[3] D. Noble, Product Review: FT-IR Spectroscopy, Anal. Chem. June 1 (1995) 381A.
[4] U. Schiedt und H. Reinwein, Z. Naturforsch. 7b (1952) 270.
[5] A.S. Teetsov, Unique Preparation Techniques for Nanogram Samples, in: Practical Guide to Infrared Microspectroscopy, H.J. Humecki (Ed.), Marsel Dekker Verlag, New York (1995).
[6] B. Hampel, Über die Eignung verschiedener Sorten Kaliumbromid für die Infrarotspektroskopie, Spectrochim. Asta 19 (1963) 1276.
[7] H. Günzler, H. Bönk, IR-Spektroskopie, Verlag Chemie, Weinheim (1975).
[8] H. Volkmann, Handbuch der Infrarot-Spektroskopie, Verlag Chemie (1972).

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