



PREPARATION OF ULTRAPURE KBr PELLET: NEW METHOD FOR FTIR QUANTITATIVE ANALYSIS

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Abstract

Fourier Transform Infrared Spectroscopy (FTIR) is a widely used technique in the analysis of commercial products. The aim of this study is to analyse the critical issues encountered preparing the KBr pellet for quantitative analyses. In order to achieve this target we analysed bulk samples for more than ten years. Thanks to this deep experience it was possible to obtain a simple and standardized method for preparation of ultrapure KBr pellet. Often the analytical error is due to an inexperienced operator who has not carefully studied the main parameters involved. The photos in this work show some examples of pellets with perfect homogeneity, transparency and good distribution: an excellent analytical result. Poor sample preparation can lead to avoidable errors in interpretation of the resultant spectrum. A little care can avoid the need for repetitious sample preparation or embarrassing errors in results. Therefore it is necessary to have an experienced operator to use this analytical method.

Keywords: Sample Preparation, KBr Pellet, IR Spectroscopy, Quantitative analysis.

INTRODUCTION

FTIR spectroscopy represents a developmental, rapid-screening method, for use in determining the presence of Asbestos in mineralogical sample and commercial products. In the last fifteen years, hundreds of samples were analysed for more than a decade and stored in the instrumental database during consultancy, research and during qualification phases conducted from labs carrying out asbestos data analysis. More specifically, over 200 workshops, carried out in 2008 and 2013, actively contributed to the national qualification circuits for FTIR technique (Campopiano *et al.*, 2018). Thanks to this deep experience it was possible to analyse and study all the critical issues during KBr pellets preparations. The KBr disk technique is a valuable sampling method in infrared spectrometry. Samples are generally ground and mix with IR transparent salt such as potassium bromide (KBr), this is usually done to reduce the concentration of the sample and obtain a better spectrum. Powders, being examined by Infrared Spectroscopy, in transmission, are generally prepared by grinding with potassium bromide (KBr) powder. The latter is then pressed into a disk. The method of preparation of a powder sample is usually determined by the knowledge required or the chemical/physical stability of the sample. KBr doesn't contain bands within the mid-IR region of the spectrum, and thus preparation as halide disks potentially loses less information. Samples dispersed in halide powder must be homogeneously dispersed, with a particle size sufficiently small to not cause scatter (theoretically < 2 microns). The strength of an IR absorption spectrum depends on the number of molecules in the beam. With a KBr disk the strength will depend on the amount and homogeneity of the sample dispersed in the KBr powder (Campopiano *et al.*, 2015; Olori *et al.*, 2017). They will even have to be varied consistent with the diameter of the disk required. The weights quoted are for the 13 mm diameter disks.

Previous methods adopted for quantitative infrared analysis of solids in KBr (potassium bromide) required pellets of reproducible or known thickness. The aim of this study is to provide a standardized procedure for KBr pellet preparation. Our innovative process grants ultrapure KBr pellets for quantitative FTIR analysis. There are three main problems preparing KBr pellets: 1) Humidity and water absorption; 2) Christiansen effect; 3) KBr impurities. To obtain an ultrapure KBr pellet it is necessary to consider and minimize all these factors. Using the alkali-halide disk technique in infrared spectrometry we saw that moisture from the atmosphere could contaminate a KBr disk, causing its recrystallization. If humidity is present, the operator will observe a critical ratio. This value depends on the fineness and structure of the KBr; Spectrophotometric-grade KBr is totally transparent to Infrared, but is hygroscopic (Van der Maas and Tolck, 1962). Absorbed moisture causes broad water absorption bands near 3400 cm⁻¹ and 1600 cm⁻¹. Powder dampness is additionally evidenced by severe clumping of the powder. The Christiansen effect appears in the IR spectrum of powders embedded in a solid, liquid or air matrix, has an apparently anomalous transmittance (Christiansen peak) of the incident electromagnetic radiations. The height appears at wavelengths that the index of refraction of matrix are equal. A change in the position of this transmission peak with matrix refractive index value is indicative of the Christiansen effect. If the effect exists, will observe a change within the position of the transmission maximum or an alteration of the profile of the optical phenomenon. Christiansen effect are often a source of error in quantitative chemical analysis of spectra. Spectral distortions caused by the Christiansen effect are often reduced by preparing the sample in other way (Xiao-dong Liu *et al.*, 2002). The overall quality of a pellet is largely dependent upon the quality of the KBr or halide salt powder used, which should always be of a spectroscopic grade of purity. Therefore, it is very important to have a KBr with high grade of purity. Regular lab-grade KBr is likely to contain KNO₃, which gives spurious peaks. It is not possible to use it (Sievers *et al.*, 1978). Clearly, IR spectra of KBr's crystals must not show absorption bands. This is primarily achieved by a high degree of the KBr

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salt purity with respect to oxygen-containing molecular anions such as: SO_4^{2-} , NO_3^- , NO_2^- etc. Aside from this, the impurity polyvalent cations M^+ (where $\text{M} = \text{Ca}, \text{Ba}, \text{Mg}, \text{Pb}$ etc.) may form complexes which are also detected in the IR spectra of KBr. Moreover, the presence of Na^+ ions degrades the structural quality of the KBr crystals. This method allows to obtain ultrapure KBr pellets for quantitative FTIR analysis (Goriletsky *et al.*, 2001).

MATERIALS AND METHODS

All bulk samples were weighted by a Sartorius scale (MC1, capacity 210g, precision 0,01 mg, SARTORIUS AG) equipped with a device to neutralize electrostatic charges. The weighted quantities were in the range 50 μg - 2mg. Each sample was mixed with about 250 mg of pure KBr previously dried in the 300 - 400 °C range in a muffle furnace (Gefran 400) for 4-5 days. The ultrapure transparent pellets of diameter 13 mm were obtained by applying a force-weight of 10 tons for about 30 minutes. IR absorbance was recorded from 4000-400 cm^{-1} . When performing measurements, the background can be measured with an empty pellet holder inserted into the sample chamber. However, background measurements on a pellet holder with a pellet of KBr only, that contains no sample, can correct for infrared light scattering losses in the pellet and for moisture adsorbed on the KBr. Before analysing the samples, in some cases, it was performed a spectrum acquisition of a blank consisting of an ultrapure KBr pellet. The analyses were carried out with the following operating conditions: acquisition interval 4000 - 400 cm^{-1} , resolution 4 cm^{-1} and 32 scans (Perkin Elmer Spectrum one). The use of a resolution of 4 cm^{-1} was appropriate for a good separation of the bands in the spectra. The optical compartment of the instrument was flushed with nitrogen before starting sample analysis. Before each scan, the sample compartment has been saturated with the same gas for about ten minutes to clear the air (Campopiano *et al.*, 2015; Olori *et al.*, 2017; Di Pietro *et al.*, 2005).

Preparation of ultrapure KBr pellet

This method takes advantage of the property that alkali halides become plastic when subjected to pressure and form a transparent sheet in the infrared region. Potassium bromide (KBr) is the most common alkali halide used in pellets. Cesium iodide (CsI) can also be used to prepare pellets in the 400 to 250 cm^{-1} low-wavenumber infrared region. Preparation method for quantitative analysis (13 mm-diameter pellets) is described below (Shimadzu, 2020).

Treatment of pure KBr

- The KBr powder must be of spectroscopic grade purity. Transfer weighed amounts of KBr powder approximately 3 - 5 g (quantity depends on the size and the extended surface of the weighing bottle) into an agate mortar.
- Grind the powders, with an agate pestle, until the sample is well dispersed and the mixture has the consistency of fine flour (control granulometry of fine flour with Stereo Microscope or better with Electron Microscope (SEM)).
- The KBr powder must be spectroscopically dry. Powder dampness is also evidenced by severe clumping of the powder. So, then dry at approximately 400 °C using a weighing bottle for three-four days in muffle furnace

(during the day, periodically, every three - four hours, move the weighing bottle to change the exposed surface and eliminate powder dampness with a micro spatula).

- After drying the powder, store it in a dryer to cool it down: prepare five pellets within 2 to 3 hours. Alternatively, it is possible to keep the KBr powder dry under an UV lamp (Osram Siccaterm - 250 W) (Figure 1) (Olori *et al.*, 2018).



Figure 1. KBr's powder (dried under an UV lamp)

Preparation of pellet

Approximately 2-3 mg sample is well mixed into 200 to 250 mg fine alkali halide powder (amount of KBr is chosen according to the thickness of the final tablet to be obtained. It is important to have a minimum thickness of 1.5 mm and a maximum of 3 mm); then finely pulverized and put into a pellet-forming die. Weigh this on a minimum 4-place analytical balance to ensure accuracy.

- Transfer weighed amounts of sample, approx. 2 mg, and KBr powder approx. 250 mg into a weighing basket (made of Teflon). The KBr powder must be of spectroscopic grade purity and be spectroscopically dry.
- Blend powders together, with an agate pestle, until the sample is well dispersed in the weighing basket and the mixture has the consistency of fine flour (this step is called comminution and isn't a grinding)
- Assemble the die, with the lower pellet polished face up.
- Transfer the ground mixture into the cylinder bore so that it is evenly distributed across the polished face of the lower pellet. Gently inserting the plunger and lightly swivelling can often achieve a flat, even surface (make sure the sample surface is level before closing the tablet)
- Insert the second pellet, polished face towards the mixture, into the bore followed by the plunger.

Option A:

- -If present, place the die assembly into a hydraulic press, between the ram and the piston.
- -Ensure that the die is firmly held in the press.
- -Connect a vacuum tube and switch on a High Vacuum pump.

- Leave the die assembly under vacuum for approximately 2 minutes. This removes air from the disk. (Some spectroscopists claim loose water is removed from the KBr and/or solvent from the sample. Others dispute this. Either way good vacuum leads to good disks)
- Increase pressure in the press to 10 tons for 13 mm die, (follow manufacturer's instructions for max pressure with other diameter dies).
- After approximately 1 minute, slowly release the pressure.
- Carefully release the vacuum, and remove the die from the press.

Option B:

- If not present, insert pellet in the mechanical press, for approximately 30 minutes, to 10 tons for 13 mm die (follow manufacturer's instructions for max pressure with other diameter dies).
- Disassemble the die, and transfer the KBr disk to an IR sample holder. Avoid touching the faces of the disk.
- Check that the disk is translucent and that the sample is homogeneously distributed in the disk (accepts good disks, rejects others).
- Measure the thickness of pellet with Palmer instrument or other similar instruments (accepts pellet with 1,5 – 3 mm thickness)
- Mount good disk holder in the spectrometer with tweezers (avoid contact with your fingers as the disk may pick up moisture) (Olori *et al.*, 2018; VDI, 2001; Health Canada, 2003).
- It's very important to pay attention to not breathe on the sample while grinding it and to not take too long since the KBr is hygroscopic. Before to assembly to hydraulic press, all other steps, for every single pellet, must not exceed 2 maximum 3 minutes.
- Wipe clean, with ethanol absolute or propanol, all equipment and all die components. Reassemble the die and replace all equipment in the desiccator cabinet (Specac, 2017).

properly ground ($\approx 2\mu\text{m}$), evenly dispersed minerals at low concentration (on the order of 0.2-0.3%) in a KBr pellet shows a linear correlation with concentration (Duyckaerts, 1959; Chester and Elderfield, 1967; Pichard and Frohlich, 1986; Frohlich, 1989). This point is very important because it provides an experimental confirmation that in given condition Lambert-Beer's law can be applied to a suspension of solid particles, as ground particles dispersed in KBr. However, errors may occur in the measurement of the intensity of the bands due to the inhomogeneous distribution of the sample in the pellet (Figure n.3).



Figure 2. Tremolite's pellet (example of perfect pellet)



Figure 3. Chrysotile's pellet (example of imperfections and inhomogeneous distributions)

RESULTS AND DISCUSSION

Five pellets were realized for every sample's typology. The two worst pellets, which showed inhomogeneities, lesions, opacities or imperfections, were rejected. For the remaining three pellets were performed six IR spectrum acquisitions for each pellet; (Figure n.2) three for each pellet side in order to mediate possible inhomogeneities invisible with naked eye. The basis for quantitative analysis of absorbance spectrometry is Lambert-Beer law (Campopiano *et al.*, 2015). For a single compound in a homogeneous medium, the absorbance at any frequency is expressed as $A = a b c$ where A is the measured sample absorbance at the given frequency; a is the molecular absorptivity, b is the absorption path length (pellet thickness) and c is the concentration of the substance. It is known that Lambert-Beer law is restricted to monochromatic light, (Van der Marel and Beutelspacher, 1976) non-interacting absorbers, very dilute solutions, absence of a Christiansen effect, (Prost, 1973) particle size smaller than wavelength used, absence of scattering, linearity of the detector, and the assumption that the slits are infinitely small. Despite all these restrictions, it has been empirically demonstrated the mid-IR absorbance of

When the sample is distributed unevenly in the pellet, the beam of the Fourier Transform Infrared (FTIR) spectrometer can fall on pure KBr regions with no test substance and this may lead to distortion of the measured intensities of the bands. The increase of voids caused by the inhomogeneous distribution of the test substance in the pellet leads to the decrease of recorded bands intensities and stronger bands decrease more significantly than weaker ones. Thus the so-called smoothing of the spectrum occurs. For an accurate preparation of pellets the particle size should not exceed $2.5\mu\text{m}$ (Xiao-dong Liu *et al.*, 2002). In general under this value, the scattering losses can be ignored (Xu *et al.*, 2001). Particle size of the sample affects the optical properties of a KBr disk. Large crystals are particularly objectionable because they produce opaque spots. Extremely fine particles are also undesirable as they absorb water quite rapidly and tend to produce disk flaking (Figure 4). So it is better have not nanometric particles. It's fundamental to check the size of particles with Stereo-Microscopy or with SEM and regrinding the KBr is the size is incorrect.



Figure 4. KBr's pellet (example of disk flaking)



Figure 5. KBr's pellet (example of transparent disk)

Regular lab-grade KBr is likely to contain KNO_3 , and other impurities which gives spurious peaks. Don't use it. Spectrophotometric-grade KBr is completely transparent to infrared radiation, but is hygroscopic. Unlike nitrates and nitrites that can be eliminated by the overheating melt prior to crystal growth SO_4^{2-} ions enter the crystal and, therefore, are considered to be the most harmful impurity. It's necessary to use a KBr that must be of spectroscopic grade purity (For example KBr Merck for spectroscopy). Total Impurities maximum accepted $\leq 0.005\%$ (insolubles) ($\text{Ba} \leq 0.002\%$ - $\text{BrO}_3 \leq 0.001\%$ - $\text{Ca} \leq 0.002\%$ - $\text{Cl} \leq 0.2\%$ - $\text{Fe} \leq 5$ ppm - $\text{IO}_3 \leq 0.001\%$ - $\text{I} \leq 0.001\%$ - $\text{Mg} \leq 0.001\%$ - $\text{Na} \leq 0.02\%$ - $\text{SO}_4 \leq 0.005\%$). Absorbed moisture causes broad water absorption bands near 3400 cm^{-1} and 1650 cm^{-1} . Powder dampness is also evidenced by severe clumping of the powder. KBr should be oven dried (as explained in materials and methods section 2.1.1) and then stored in a desiccator or under UV lamp to eliminate moisture interference. Uniform distribution of a sample in the KBr matrix is necessary for good results. If the spectrum contains bands which have a flattened turning point and do not reach 0 % T, this is caused by a poorly dispersed sample or holes in the disk. Check the disk visually and if necessary repeat the preparation. Sloping baseline: This is usually due to a poorly dispersed sample. A transparent disk is excellent (Figure n.5). A translucent disk will work (Figure n.6). An opaque disk is probably useless and rejected. If the disk breaks on removal from the die, this indicates that the disk is too thin caused by too little powder, or procedure of extraction has been wrong or too much pressure for too long (Figure n.3). Remedy this effect by increasing the sample load. Also check that the correct pressure is used. Therefore it is important to measure the thickness of the disc and be gentle when extracting the pellet. If the disk is not translucent, this could have numerous causes: uneven distribution of powder in die, too much sample, too much KBr powder, poorly dispersed sample, water in disk, pellet pressed at too low pressure or for too short a time. All faults can be repaired by using the new method of preparation of ultrapure KBr (described in section 2). If the spectrum contains bands which have a flattened turning point and do not reach 0 % T, this is caused by a poorly dispersed sample or holes in the disk. Check the disk visually and if necessary repeat the preparation. Sloping baseline: This is usually due to a poorly dispersed sample (Figure n.3). The disk turns brown. This could be due to the sample being an oxidising agent. Often rapid heating can oxidize the KBr powder to KBrO_3 , making a brown discoloration. Check the spectrum for halide degradation and re-examine as a mull if possible (Shimadzu, 2020). It is necessary, to heat with progressive thermal steps (to eliminate this problem) (Olori *et al.*, 2007).



Figure 6. KBr's pellet (example of translucent disk)



Figure 7. Chrysothile's pellet (example of good distributions and transparencies)

Some substances are too hard (polymers) or too crystalline (for example Anthraquinone) to disperse properly. The latter can also cause bands to appear like a first derivative spectrum. This is due to refractive index changes and is known as the Christiansen Effect. The trouble is much low by using this method. The baseline of the transmission spectrum may drop to the left: if the sample has a rough surface or contains inorganic compound dust. This is caused by the scattering of infrared light on the sample surface and this effect is greater for the shorter wavelength. As a result, an IR spectrum affected by dispersion drops more towards the short wavelength end (high wave number). Therefore disc surface must be totally smooth (Figure 7). All the pellets in figure 2, 5 and 7 are prepared with Option B and the results are excellent (Olori *et*

al., 2018). The ideal method is option A but not all laboratories have hydraulic press.

CONCLUSION

Spectroscopic methods have been widely used in the quantitative analysis of asbestos. The validity of the quantitative information depends on the history of the sample. Very often the main problem is associated with the representative sampling rather than the specified instrumental technique (Pierini *et al.*, 1995; Olori *et al.*, 2018; Klick *et al.*, 1967; Anbalagan *et al.*, 2009). Poor sample preparation can lead to avoidable errors in interpretation of the resultant spectrum. A little care can avoid the need for repetitious sample preparation or embarrassing errors in results. Therefore, it can be of great importance to have a standardized and effective procedure for the preparation of the KBr pellet (Olori *et al.*, 2018). Any solid sample which can be reduced to a fine powder and which does not react with KBr can be examined using the pressed disk method. In addition to crystalline materials as asbestos, rubbery or plastic samples can be ground with ultrapure KBr method. We obtained the best results minimizing the three main factors that affect the preparation: humidity; Christiansen effect and KBr impurities. The other causes do not significantly affect the transparency, homogeneity and uniform dispersion of the tablet: therefore are negligible. The advantages of this method are: the perfection of the pellet; the results obtained in the quantitative analyses; (Campopiano *et al.*, 2015) the total elimination of the main errors; the background smoothing; the possibility of not using the hydraulic press for preparation and not using nitrogen flushing for analysis (option A); the possibility to low the limit of detection (LOD) and the limit of quantification (LOQ) for asbestos and other compounds (Olori *et al.*, 2018; VDI, 2001). The disadvantages are: preparation time (about a week); an expert operator who has carefully studied the main parameters involved is indispensable to obtain the maximum analytical result; must follow all the steps of the procedure in a consequential manner; it is essential to have, available, all the equipments described in the analytical method.

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