

SWeRF_{CS}

Size Weighted Respirable Fraction of Crystalline Silica

A method for evaluating respirable crystalline silica content and related hazard potential in bulk materials

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1.1 Introduction

Dust is a potential health hazard when it is inhaled and when the particles are small enough to enter deep into the gas exchange regions of the lungs. Not every inhaled particle will penetrate into the alveoli but the probability is higher for a smaller particle than for a larger one.

Definition: A respirable particle is a particle that is small enough to be able to penetrate into the unciliated airways. [1] ref to EN481

1.2 Fraction of respirable particles

Consider two different samples of the same material. Both samples consist only of particles with an aerodynamic diameter smaller than 16 μm but have a different size distribution (fig.1 and 2).

According to EN 481 any of these particles have a chance to reach the alveoli when inhaled. This means that both samples are made up entirely of particles which fall in the respirable size range.

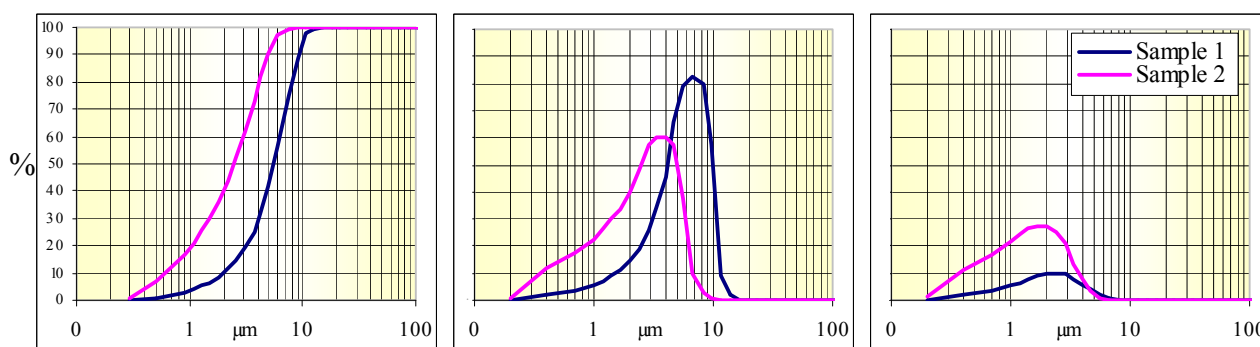


Fig.1.Cum. size distribution

Fig.2. Size distribution

Fig.3. SWeRF size distribution

1.3 Size Weighted Respirable Fraction (SWeRF)

Although both samples are made up entirely of respirable particles, it is clear from the figures that sample 2 contains more fine particles with more chance to enter deep into the lungs when inhaled. Therefore sample 2 is potentially more dangerous. Particles with an aerodynamic diameter of e.g. 1 and 10 μm are both considered being respirable. The difference is that the particle of 1 μm has, according to European standard EN 481, a probability of 97.1 % reaching the alveoli, as compared to 1.3 % for the particle of 10 μm .

By giving relatively more weight to the finer particles, it is possible to express the difference in potential health hazard. The SWeRF of a particulate material is calculated by combining the amount of particles of a certain size, with its probability of reaching the alveoli when inhaled, i.e. the fraction of particles of 1 μm is multiplied by 97.1 % and the fraction of particles of 10 μm is multiplied by 1.3 % (EN 481). After doing this for all size fractions (see fig.3), this adds up to a SWeRF of 16.4 % for sample 1 and 50.7 % for sample 2. This indicates that, when inhaled under the same conditions, 3 times more dust of sample 2 would reach deep into the lungs as compared to sample 1.

SWeRF can be understood as the physical fraction of respirable particles (e.g. 0.1 or 10%) or their size distribution

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2. Scope

Crystalline silica (CS) in a material can cause silicosis when particles get airborne and are inhaled. Although "normal" dust is not harmless, extra care should be taken with materials containing crystalline silica. As long as a product is kept in a sealed bag, there is no danger because no dust is released. The industries handling industrial minerals have methods to control airborne dust (CS) but there has been no easily quantified method available to assess the potential hazard of respirable CS in a bulk material.

SWeRF was proposed as indication for the potential hazard of a product forming respirable dust when handled. It was also proposed to combine the SWeRF of a bulk material and its CS content to determine the SWeRF_{CS} by multiplying these two factors to indicate the potential hazard of respirable crystalline silica (RCS) in the bulk material.

The scope of this investigation is to assess the validity of this proposal.

3. Experimental procedure

A series of tests were performed by an external lab (reference) to demonstrate whether the results of the tests and the calculated SWeRF_{CS} using the SWeRF and CS content of a bulk material are comparable.

Since no standard method is available to determine the SWeRF of samples, a new test was developed. The respirable fractions of the samples were determined using sedimentation in a liquid. The samples were dispersed in a liquid and left to settle for a certain period after which the upper part (with the particles of interest) was separated; the time of sedimentation was calculated based on the principles described below. The extracted particles are dried, weighed and analysed for crystalline silica content. The results were compared with the calculated SWeRF and SWeRF_{CS}

3.1 Sedimentation in liquid

When mixed in a liquid, small particles will settle more slowly than larger ones and will therefore remain longer in suspension. The settling velocity of a particle in liquid is described by Stokes' law. Small particles also have a high probability to enter deep into the lungs when inhaled. This is described by EN 481 and based on the aerodynamic diameter of the particles. We assume that settling of particles in air (aerodynamic diameter) and settling of the same particles in liquid are proportional. Combining these two principles makes it possible to separate the SWeRF of a sample by means of sedimentation in a liquid. This also makes it possible to determine the amount of CS in the SWeRF of a material since the SWeRF is now physically separated from the rest of the sample. The method is based on dispersing a sample in liquid in which the larger particles settle more rapidly, leaving a fraction of finer particles in the top part of the suspension. After a certain time of sedimentation, the fraction in the top part of the suspension will approach the fraction of particles as would be separated by the lungs (according to EN 481). To determine the SWeRF, the top part needs to be separated from the rest of the suspension.

The appropriate time of sedimentation and the depth of the sample (h) to be extracted can be calculated by equating Stokes' law with the distribution function of EN 481.

3.1.1 Stokes' law

A spherical particle will accelerate to a constant settling velocity according to:

$$v = d^2 * \frac{(\rho_s - \rho_m) * g}{18 * \eta} \quad [\text{Equation 1}]$$

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In which:

v = settling velocity of the particle in m/s

ρ_s = density of the particle in kg/m³

ρ_m = density of the medium in kg/m³

g = acceleration (gravitation) in m/s²

d = diameter of the particle in m

η = viscosity of the liquid in kg/(m.s)

3.1.2. Respirable fraction according to EN 481

EN 481 (Workplace atmospheres: size fraction definitions for measurements of airborne particles) describes the convention for the respirable fraction of airborne particles. It describes how smaller particles have a higher probability to reach the alveoli than larger ones. A graphical representation of this function is given for quartz (density 2650 kg/m³) in fig. 4.

3.1.3. Calculation of the time of sedimentation

The probability curve of EN 481, describing the probability of respirable particles reaching the alveoli, is not the same as the function that describes the fraction of particles remaining in suspension after sedimentation. However, by choosing the appropriate time of sedimentation, the separation by sedimentation will approach the separation of particles in the lungs. Fig 4. shows the effect of different times; 1h59 min being the time of sedimentation that best approaches EN 481 in this example. This example is for quartz in water with the height of the column to be separated set at 10 cm.

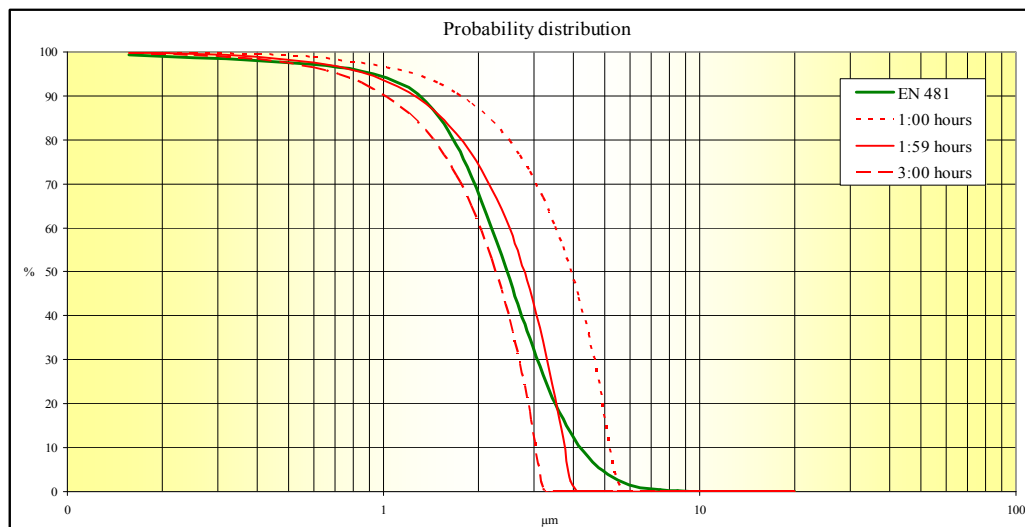


Fig. 4. Probability distributions for quartz for EN 481 and separation in liquid at different times of sedimentation.

The size distribution of a sample is given in fig.5. The size distribution of the SWeRF of this sample, as calculated using EN 481, is represented by the green curve. The surface under the curve represents the amount of the SWeRF. Separating the SWeRF of this sample using sedimentation will give a distribution and amount as represented by the red curve. By calculating the appropriate time of sedimentation it is possible to separate a fraction from a sample that approaches very well the SWeRF as calculated EN 481 both in amount and size distribution.

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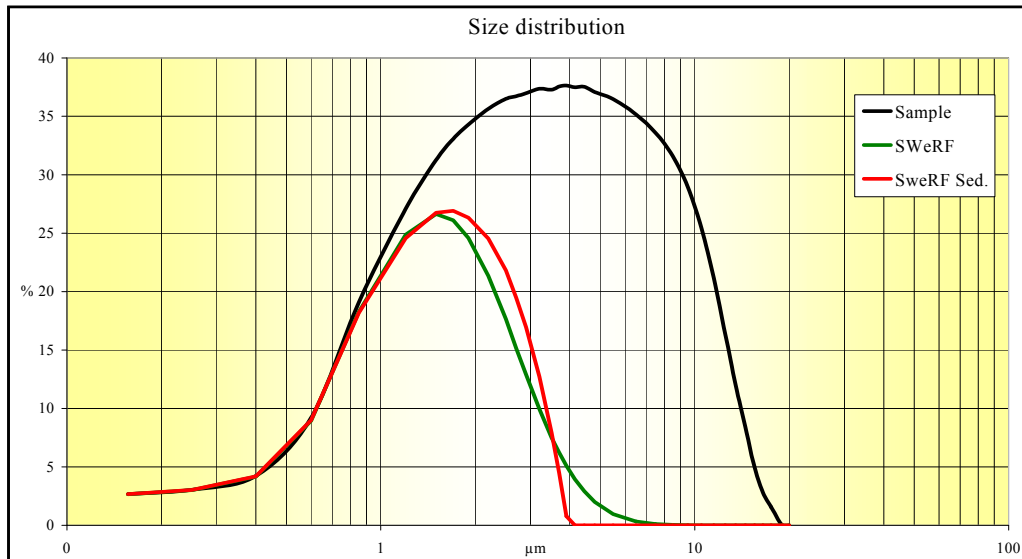


Fig. 5. Size distributions of a sample by light scattering and of the corresponding SWeRF's (EN 481 and sedimentation).

The time of separation by sedimentation can be calculated according to equation 2. This equation is the result of equating the probability function from EN 481, integrated for particles up till 100 μm, with the integrated probability that particles remain in suspension for a certain time.

$$t = h * \frac{18 * \eta}{(\rho_s - \rho_m) * g} * \frac{4}{9} * \left(\frac{\sqrt{\frac{\rho_s}{\rho_{\text{water}}}}}{\left(\sum_{D_{\text{Aero}}=0}^{D_{\text{Aero}}=100\mu\text{m}} (\text{EN 481}) \right)} \right)^2 \quad [\text{Equation 2}]$$

t= time (s) at which sedimentation in liquid equals separation according EN 481

h= height of the column of liquid which is extracted (m)

η= dynamic viscosity of liquid (kg/ms)

g= acceleration (gravitation) m/s²

ρ_s= density of the solid particles kg/m³

ρ_m= density of the liquid kg/m³

D_{Aero}= aerodynamic diameter (μm)

$$\sum_{D_{\text{Aero}}=0}^{D_{\text{Aero}}=100\mu\text{m}} (\text{EN 481}) = 4,2818 \times 10^{-6} \text{ m}$$

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4. Experiments

The following series of tests were done:

1. Quartz flour samples
2. Addition of quartz to barite
3. Several different minerals

The size distributions of the samples were provided by the producers of the products.

4.1. Comparison of calculated and measured SWeRF.

Quartz samples were used to check the validity of the assumption that the SWeRF of a sample can be calculated using its size distribution. Three different quartz flour samples and one sample of fine sand were analysed.

		Quartz 800	Quartz 600	Quartz W3	Sand
D50	µm	2.3	3.0	90.0	150
Sedimentation in water					
SWeRF	%	64.21	41.86	2.91	<0.01
Quartz	%	92.60	91.56	82.47	
SWeRF cs	%	59.46	38.33	2.40	0.00
Calculated					
SWeRF	%	52.46	42.17	3.53	0.0
Quartz	%	100	100	90	100
SWeRF cs	%	52.5	42.2	3.18	0.0

Table1: Comparison of calculated and measured SWeRF in samples of quartz.

The SWeRF by sedimentation and the calculated SWeRF are in the same order of magnitude.

4.2. Effect of density and recovery of quartz from a mixture: addition of quartz to barite.

Quartz and barite have very different densities. Known quantities of quartz were added to a barite that contained no quartz. The objective was to find out if the added quantity would be recovered by the sedimentation technique and if this matches with the calculated SWeRF's of these mixtures. The size distributions and the added amounts of quartz 600 were used to calculate SWeRFcs of each mixture. The first test showed very poor results because of the agglomeration of barite and quartz. This resulted in very low values for the SWeRF determined by sedimentation. This was remedied by adding a small quantity of a dispersant (sodium hexameta phosphate). The results are in table 2.

Addition of Quartz flour to barite				
Effect on SWeRF _{CS} using sedimentation method				
	EN 481 Calculated	Sedimentation method		
% Q	SWeRF _{CS}	SWeRF	% Quartz (res.)	SWeRF _{CS}
0	0,00	0,00	0,00	0,00
25	11,25	34,58	28,29	9,78
50	21,91	38,07	58,25	22,18
75	31,97	40,82	79,43	32,43
100	41,43	41,80	91,89	38,41

Table 2: Addition of Quartz flour to barite

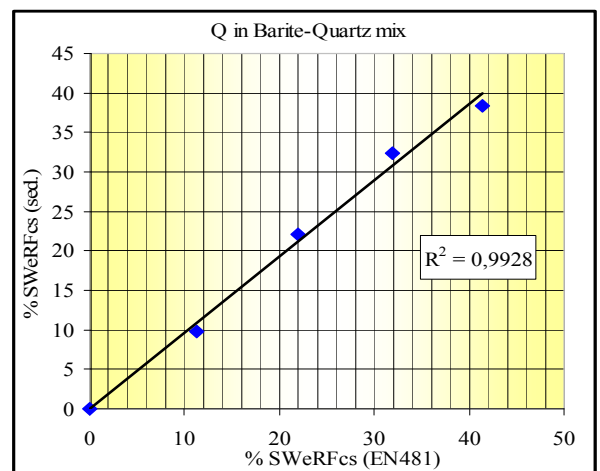


Fig. 6: Correlation

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Both methods show a very good correlation. Quartz could be recovered proportionally from a mixture containing a mineral of higher density.

4.3. SWeRF_{CS} in industrial minerals

The calculated SWeRF_{CS} of a mineral product is based on the principle that the crystalline silica has the same size distribution as the other minerals in the product. Because of the high hardness and absence of cleavages, quartz is tougher than most minerals and will most likely be rather more present in the coarser fraction. This would result in an overestimation of the calculated SWeRF_{CS}. A series of tests with different industrial minerals were performed to verify this.

Most sedimentations were performed in water, which is not necessarily the right medium for all minerals. A sample should completely deagglomerate in the medium; it should not dissolve, swell or disintegrate in it nor should it react with it. E.g. clays or cement should not be analysed in water. This is why some of the minerals were analysed using both water and methanol. The results are displayed in table 3.

		Feldspar	Limestone	Leucophyllite	Clay 1	Diatom Earth Calcined
D50		14.6	3.0	17.2	3.1	10.3
Sedimentation in water						
SWeRF	%	8.10	0.37	1.37	25.92	48.04
Q	%	8.94	0.79	29.26	8.01	1.38
SWeRF _{CS}	%	0.72	0.00	0.40	2.08	0.66
Sedimentation in Methanol						
SWeRF	%	10.32	26.97	0.30	0.29	29.00
Q	%	20.28	0.75	40.45	12.07	6.97
SWeRF _{CS}	%	2.09	0.20	0.12	0.04	2.02
Calculated						
SWeRF	%	12.2	43.2	15.4	38.1	17.5
Q	%	26	1.85	30	36	10
SWeRF _{CS}	%	3.17	0.80	4.62 *	13.72	1.75

* Sedigraph

Table 3. Overview results SWeRF_{CS} industrial minerals

5. Discussion of the results

5.1. Comparison of calculated and measured SWeRF.

The sand sample contained fine particles but the concentration was too low to be meaningful. Sample Quartz 600 and W3 gave reasonable results. Only Quartz 800, the finest sample, gave a higher value than could be expected based on the grain size distribution given by the supplier. A SWeRF of 64.2 % was found whereas only 52.5 % was calculated. Further analyses with a different laser diffraction instrument showed improved results (57.8 %). The size analyses were done using laser diffraction, which might not be the best technique for such a fine material.

5.2. Addition of quartz to barite

Known amount of Quartz 600 were added to a sample of barite. The SWeRF_{CS} were calculated using the size distributions of the mixtures and the density of quartz. These results were compared

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with the results from the sedimentation analyses. As can be seen in fig. 6 both methods show a very good correlation.

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5.3. SWeRF_{CS} in industrial minerals

5.3.1 Feldspar

Sedimentation in water resulted in lower SWeRF than sedimentation in methanol and calculated. Combined with the fact that different concentrations of quartz were found in the SWeRF leads to the conclusion that the sample was not completely deagglomerated. The results in methanol are better especially when taking into account that the amount of quartz in the bulk sample determined by RPS was 22 %.

5.3.2 Limestone

Sedimentation in water resulted in a much lower SWeRF than sedimentation in methanol and calculated. The sample in water was clearly agglomerated. In methanol the SWeRF was higher but still lower than calculated.

5.3.3 Leucophyllite

Sedimentation in both water and methanol resulted in a much lower SWeRF than calculated. The sample was clearly agglomerated in both water without additives and methanol.

5.3.4 Clay 1

It is known that clay will not deagglomerate in water without additives; the size distribution analysis was done dry. It was expected to find a higher SWeRF in water than calculated and a similar in methanol. However, both results came out much lower, which indicates agglomeration.

5.3.5 Diatom Earth Calcined

In contrast to the other minerals the SWeRF in both water and methanol are higher than the calculated. This is probably due to the porous nature of the mineral. An extra size distribution analysis using the Sedigraph resulted in a higher calculated SWeRF, which was closer to the SWeRF determined by sedimentation.

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6. Conclusions

Many of the samples showed agglomerations and settled too fast. But this could be improved as was shown in the test with barites and quartz. It is essential that for sedimentation of a sample, a suitable liquid should be chosen. The particles should remain in the same state as if airborne. They should not agglomerate nor disintegrate in the liquid.

Quartz showed no agglomeration and a good correlation was found between the calculated $SWeRF_{CS}$ and the $SWeRF_{CS}$ determined by sedimentation.

A series of tests was done at which a known quantity of quartz was added to a sample of barite. Both the calculated and the $SWeRF$ (sedimentation) resulted in the same level and showed a very good correlation. This means that, at least in this mineral, calculation of the $SWeRF_{CS}$ is a valid method.

For the mineral Feldspar we can conclude the same when methanol is chosen as the medium for sedimentation. With a dispersant added, water should be suitable to be used as sedimentation medium as well.

For calcined diatomaceous earth the calculated $SWeRF$ can be used when a Sedigraph is used to determine the size distribution.

For the other minerals more investigation is needed namely to find a suitable way of deagglomeration. Only then a valid conclusion can be drawn if the $SWeRF_{CS}$ for these minerals might be determined by calculation.

The $SWeRF$ of a product is one single number, which makes it ideal for comparing different materials on their potential health hazard and possibly for labelling.

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Annex 1

Separation of SWeRF by method of sedimentation

1. Principle of the method

A sample is dispersed in a liquid and left to settle. Small particles will settle more slowly than larger ones and will therefore remain longer in suspension. After a certain period of time the upper part (with the respirable particles) is decanted. The time of sedimentation can be calculated using the following equation, which is based on Stokes' law and the convention described in EN 481.

$$t = h \times \frac{18 \times \eta}{(\rho_s - \rho_m) \times g} \times \frac{4}{9} \times \left(\frac{\sqrt{\frac{\rho_s}{\rho_{\text{water}}}}}{\left(\sum_{D_{\text{Aero}}=0}^{D_{\text{Aero}}=100\mu\text{m}} (\text{EN 481}) \right)} \right)^2 \quad [\text{Equation 1}]$$

t = time (s) at which sedimentation in liquid equals separation according EN 481

h = height of the column of liquid which is decanted (m)

η = dynamic viscosity of liquid (kg/ms)

g = acceleration (gravitation): 9.81 m/s²

ρ_s = density of the solid particles kg/m³

ρ_m = density of the liquid kg/m³

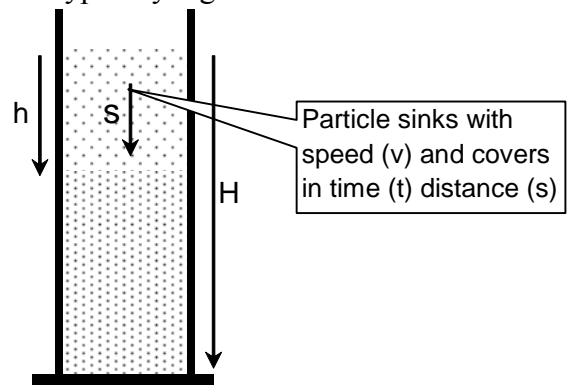
D_{Aero} = aerodynamic diameter (μm)

$$\sum_{D_{\text{Aero}}=0}^{D_{\text{Aero}}=100\mu\text{m}} (\text{EN 481}) = 4,2818 \times 10^{-6} \text{ m}$$

2. Method

Water is a good medium for separation by sedimentation, however the sample needs to be completely deagglomerated. It should not dissolve, swell or disintegrate in it nor should it react with it. E.g. clays or cement should not be analysed in water but rather in an alcohol.

1. Prepare the sample by weighing it (M, mg) and dispersing it in 50 ml of liquid in a 100 ml beaker. Treat it in an ultrasonic bath until completely deagglomerated. Add if necessary a suitable dispersant to keep it from flocculating or coagulating (e.g. Calgon, TSPP, ...). The volume of solids should be maximum 1 % of the volume of the total liquid to ensure undisturbed sedimentation of the separate particles. Typically 5 grams.
2. Pour the dispersed sample in a 250 ml cylinder and replenish the cylinder up till 250 ml and homogenise.
3. Place the cylinder in a location where it is free from effects that could cause currents in the liquid and leave to settle for the calculated time.
4. Determine the depth of the liquid column; H (mm)
5. After the calculated time, remove h (mm) of the top layer of liquid using a pipette;
6. Determine the weight of suspended material by evaporation the liquid; m (mg).



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The SWeRF of the sample can be calculated using equation 2

$$\text{SWeRF} = \frac{H * m}{h * M} * 100 \% \quad [\text{Equation 2}]$$

The content of crystalline silica of this separated material can be determined using techniques such as XRD or IR. The SWeRF_{CS} of the sample is calculated using equation 3.

$$\text{SWeRF}_{\text{CS}} = \text{SWeRF} * \% \text{CS} \quad [\text{Equation 3}]$$

It should be noted that for determining the SWeRF of a material, the density of this material should be used to calculate the time of separation by sedimentation. If the SWeRF_{CS} is required, the density of quartz, (or cristobalite) should be used.

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Annex 2

Quartz determinations on the original samples by RPS

Method: IR, KBr tablet conform NIOSH 7602

Table 1 Results

RPS no.	Sample	Quartz (%)
001	Leucophyllite (Talc)	38,07
002	Limestone	1,3
003	Quartz 800	101,6
004	Quartz 600	96,2
005	Quartzsand	-
006	Barite	0,110
008	Feldspar	22,0
009	Clay 1	36,3
011	Diatom Earth Calcined	5,4
012	Diatom Earth Uncalcined	< 0,1
013	Quartz W3	80,7

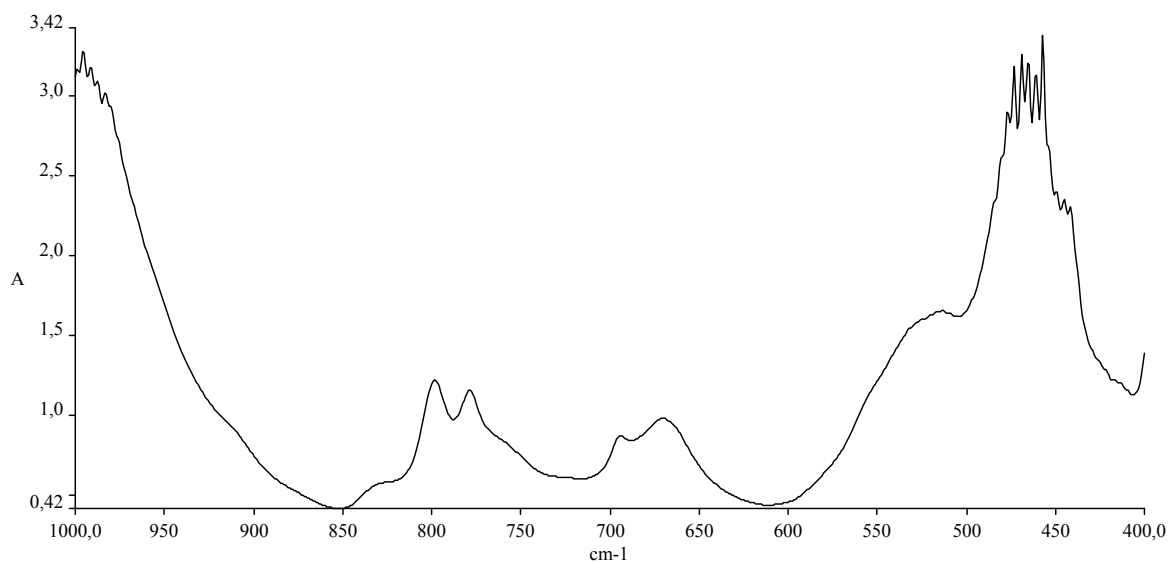
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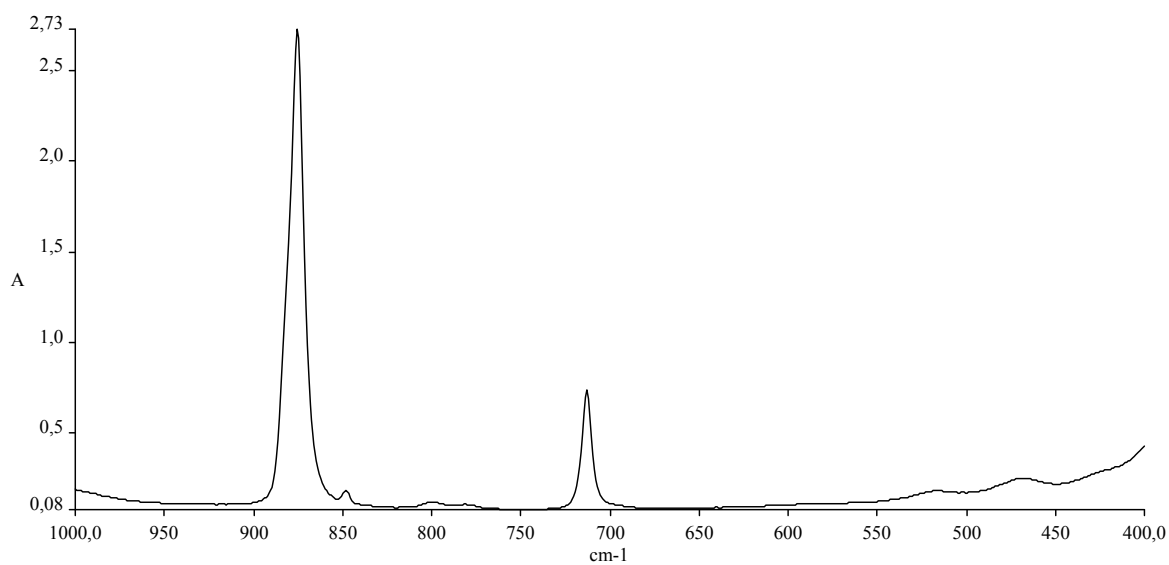
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Annex 3: infra red results

Sample Leucophyllite, RPS no. 07050317-001



Sample Limestone, RPS no. 07050317-002

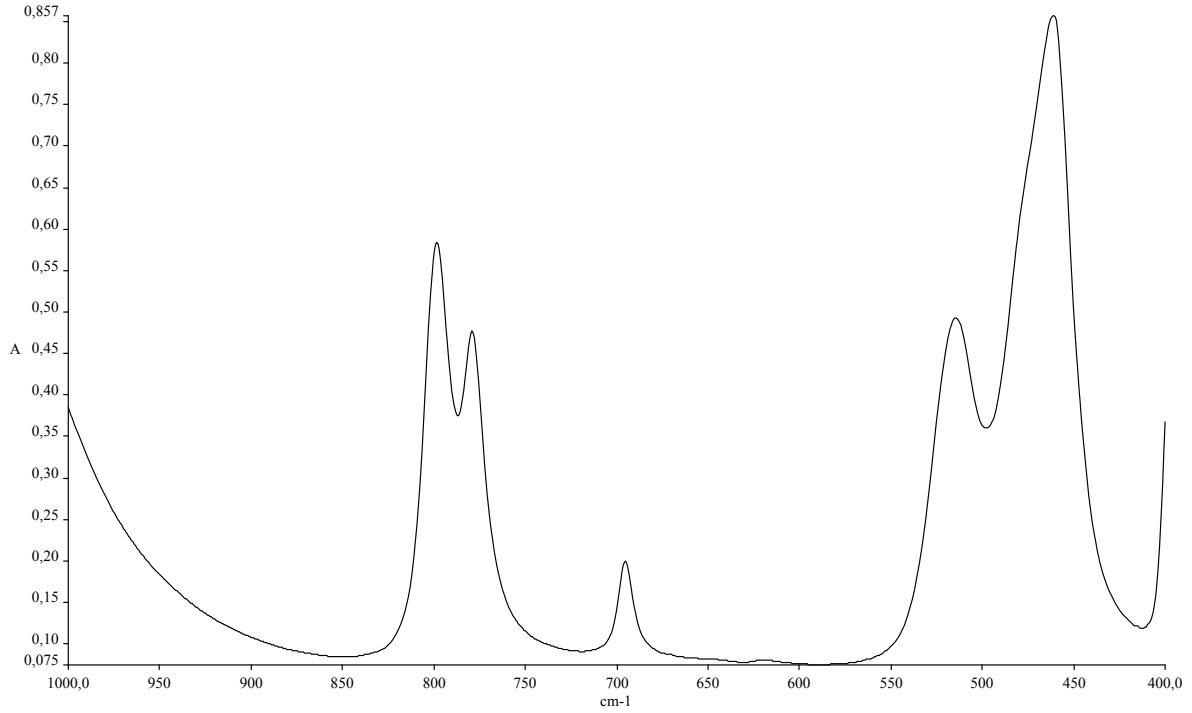


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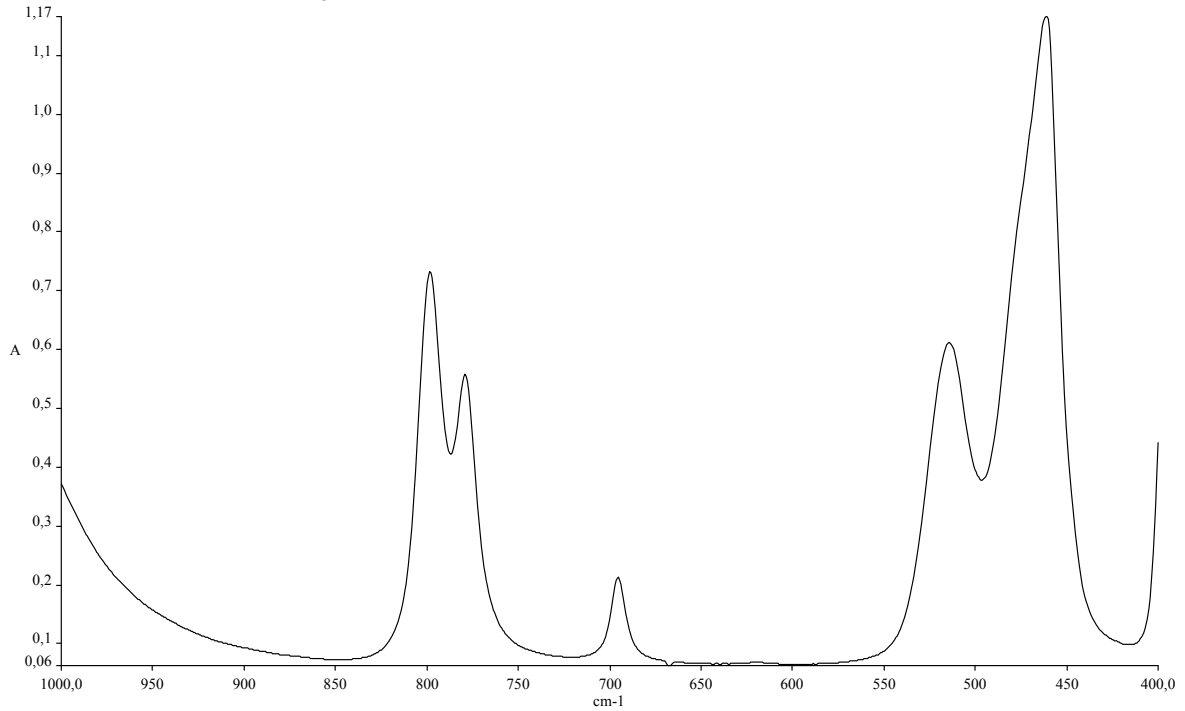
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Sample Quartz 800, RPS no. 07050317-003



To compare with scan of 500 µg quartz SRM 1878a

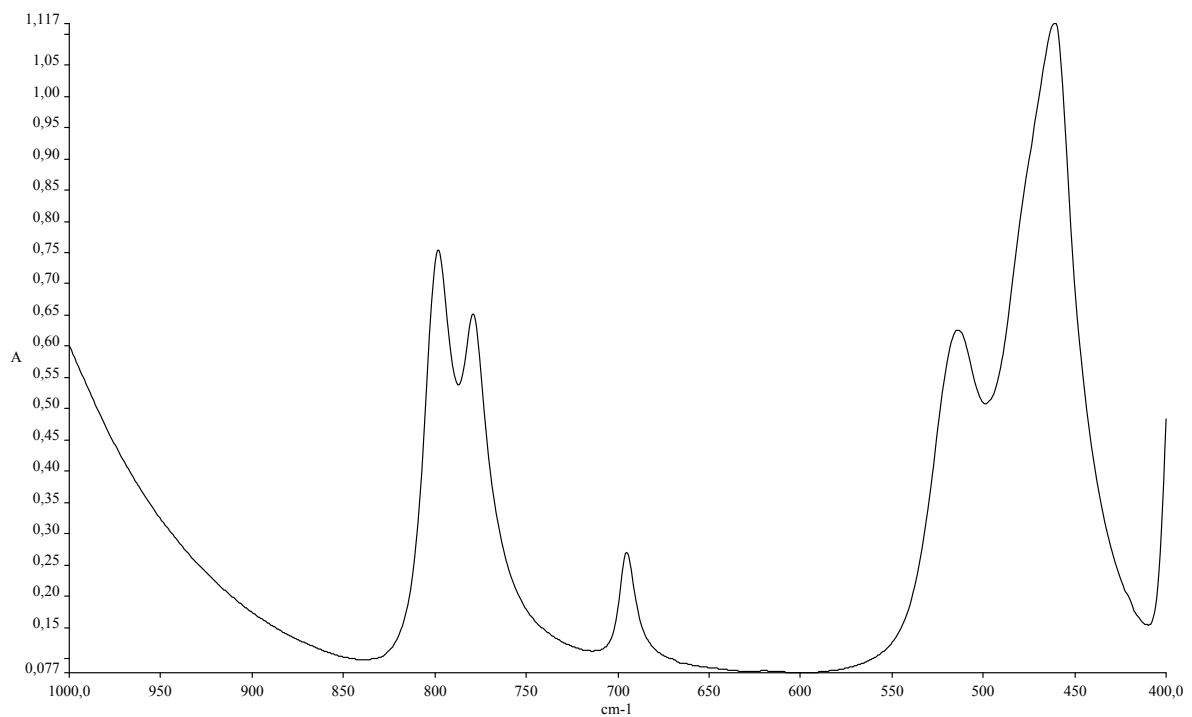


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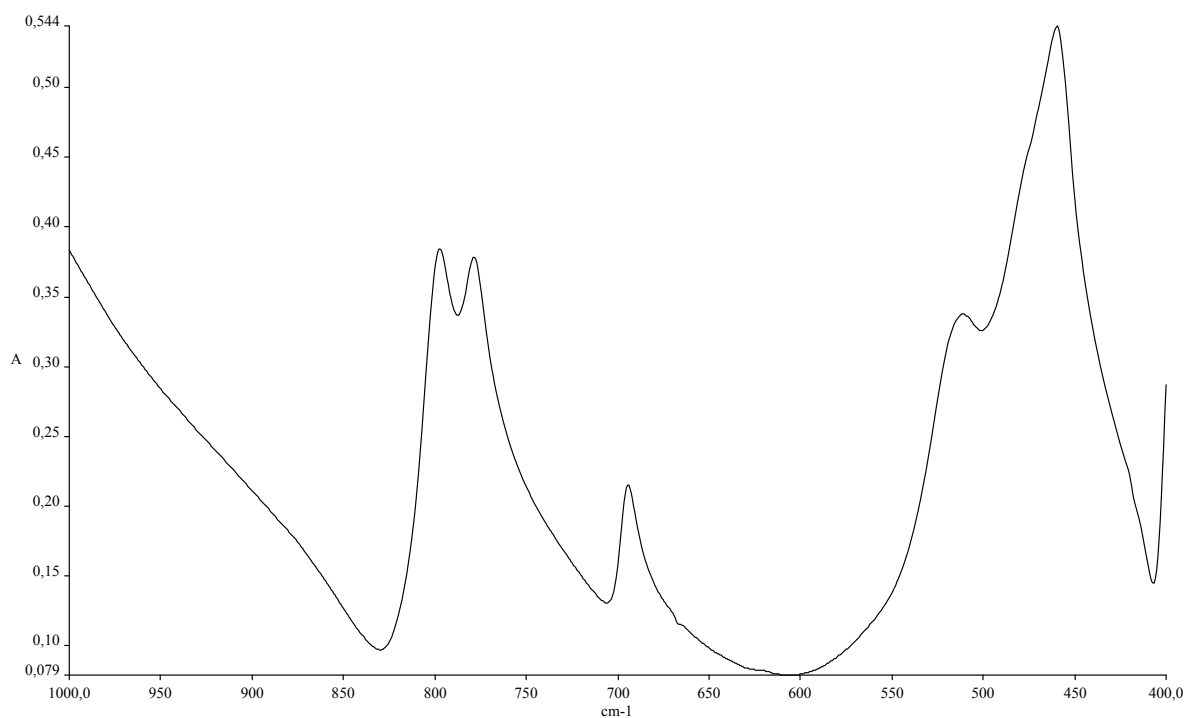
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Sample Quartz 600, RPS no. 07050317-004



Sample Quartz W3, RPS no. 07050317-013

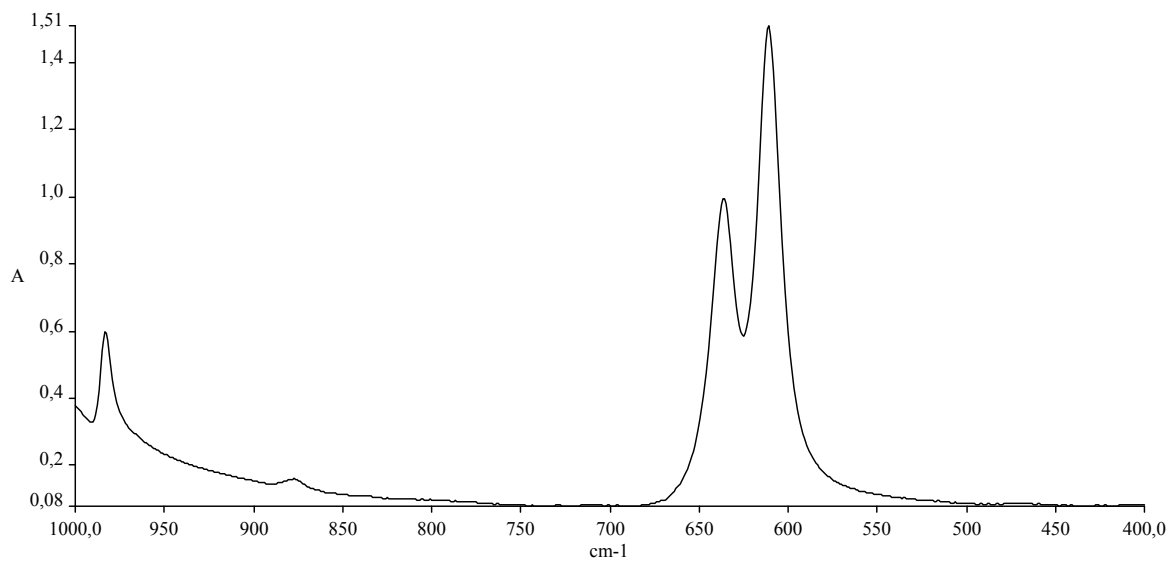


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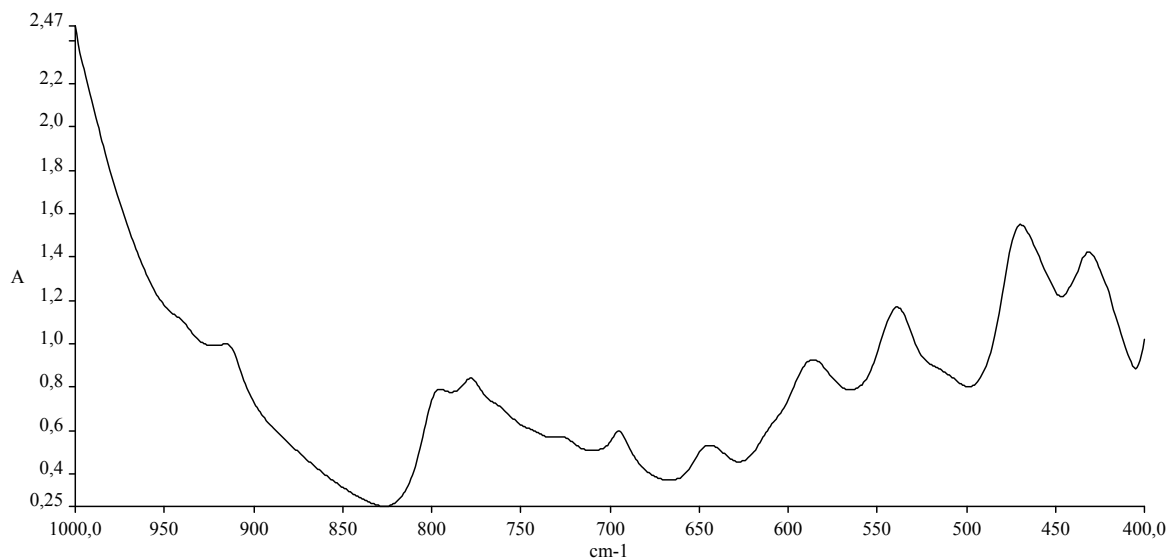
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Sample Barite, RPS no. 07050317-006



Sample Feldspar, RPS no. 07050317-008

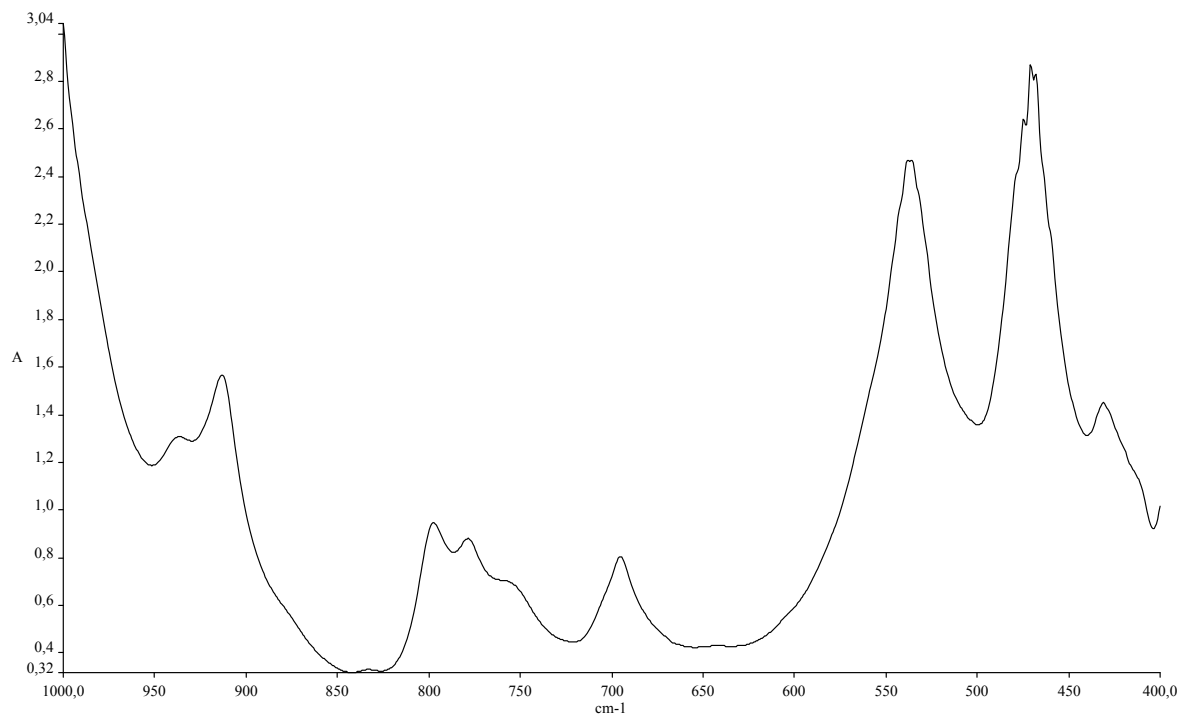


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Sample Clay 1, RPS no. 07050317-009

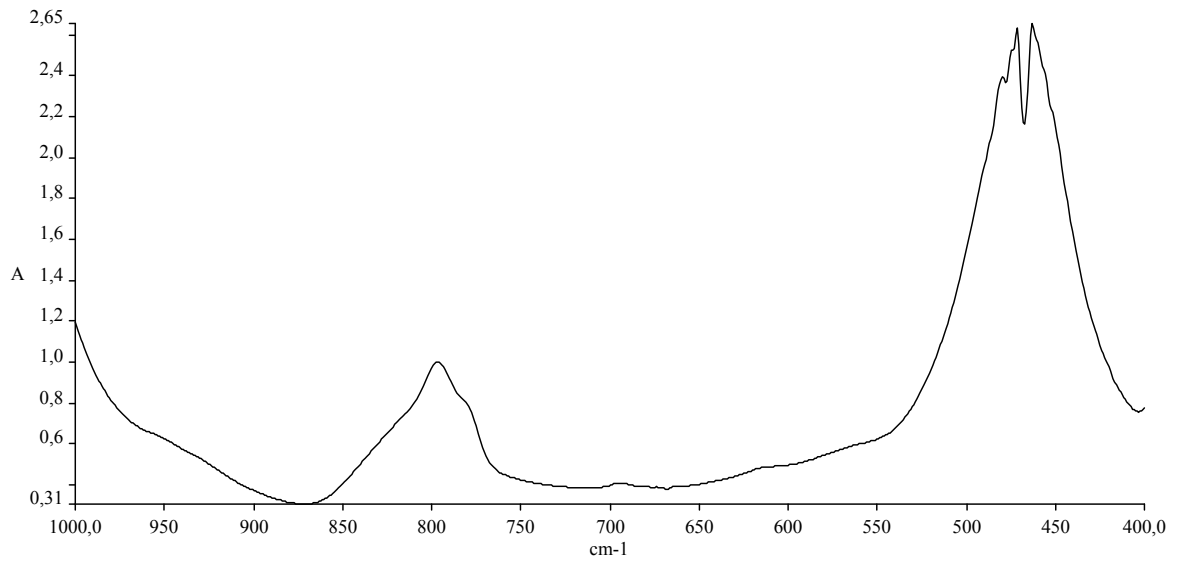


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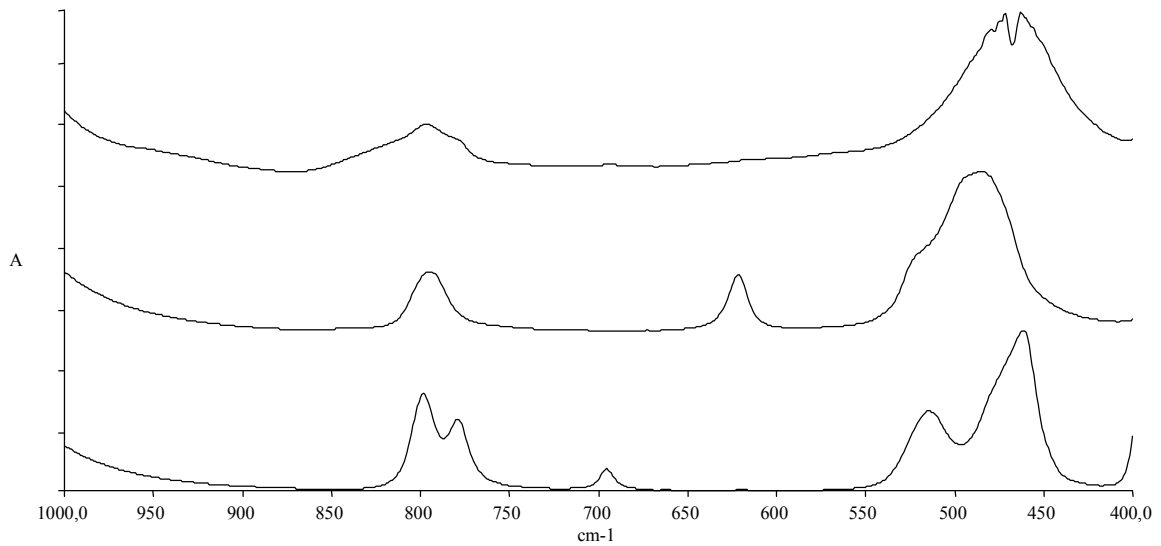
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Sample Diatom Earth Calcined, RPS no. 07050317-011



Sample Diatom Earth Calcined, RPS no. 07050317-011 circa 2000 µg (upper), circa 500 µg cristobalite (middle) and 500 µg alpha-quartz (lower)



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