

*Commutability of certified reference
materials at the nano-scale*

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Commutability of a reference material (RM)

VIM 3 (ISO Guide 99:2007): property of a RM, demonstrated by the closeness of agreement between the relation among the measurement results for a stated quantity in this material, obtained according to two given measurement procedures, and the relation obtained among the measurement results for other specified materials.

Note 1: The RM in question is usually a calibrator and the other specified materials are usually routine samples.

Note 2: The measurement procedures are the one preceding and the one following the RM in a calibration hierarchy.

Note 3: The stability of RMs is monitoring regularly.

Background for commutability evaluation

To select a necessary RM, a lab developing an IHRM or analysing a sample compares expected composition and physico-chemical parameters of the sample (or the IHRM) and those of RMs of the **same nature**, available in the market.

One can say intuitively that **100% commutability** is achieved when all the sample and the RM characteristics **coincide** entirely. In the other extreme case, the commutability is totally absent (0%) when the sample and the RM are **different substances** or materials and/or when the analyte is absent in the RM.

Score

In non-extreme cases, a lab considers a RM to be more commutable/adequate if the RM composition and properties are **as close as possible** to the ones expected for the sample. Such understanding of the commutability/adequacy can be reflected in the following score:

$$A = 100 \prod [(\min(c_{i,S}, c_{i,RM}) / (\max(c_{i,S}, c_{i,RM})))^{a_i}], \%$$

where a_i is the sensitivity coefficient: for analytes $a_i = 1$, for not interfering matrix components or parameters $a_i = 0$, for others a_i should be defined in the range of $0 < a_i \leq 1$ based on the knowledge of the analytical process, $i = 1, \dots, n$.

The score values

It is not important here if $c_{i,s}$ is the smallest and $c_{i,RM}$ - the largest, or vice versa. If only one component (analyte) is considered, $n = 1$, $a_1 = 1$ and the score is equal to

$$R_1 = \min(c_{1,s}, c_{1,RM}) / \max(c_{1,s}, c_{1,RM}) \text{ in } \%, \text{ i.e. } A = 100R_1.$$

Since the component concentrations c_i in a routine sample and RM should not differ by more than a factor of two, the acceptable values of the score in this case is $A \geq (100/2) = 50\%$.

I.Kuselman et al. *Accred. Qual. Assur.* (2007) 12:563

I.Kuselman & A.Fajgelj. *Pure Appl.Chem.* (2010) 82/5:1099

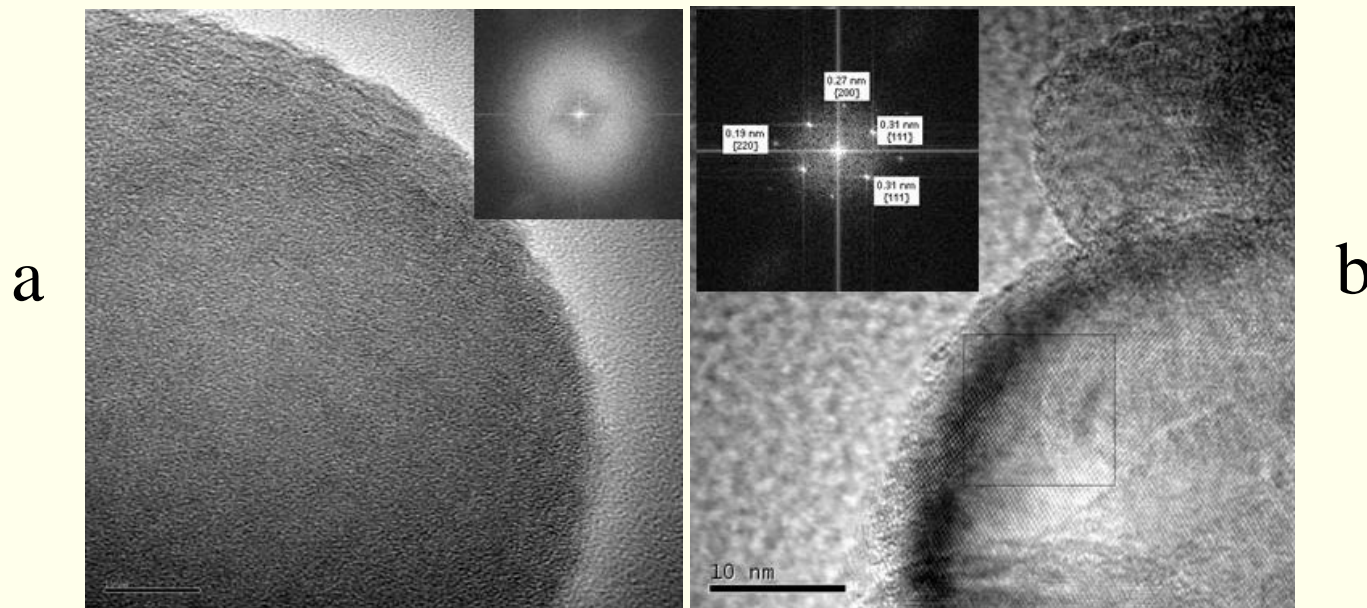
At the nano-scale

When RMs are applied for characterization of **nano-dimensional** objects, adequacy of their surface compositions, rather than of their matrixes, may contribute to the measurement uncertainty.

Moreover, the surface match at the nano-scale can allow even use of inadequate RMs, i.e., RMs with **another matrix** than of the object under characterization.

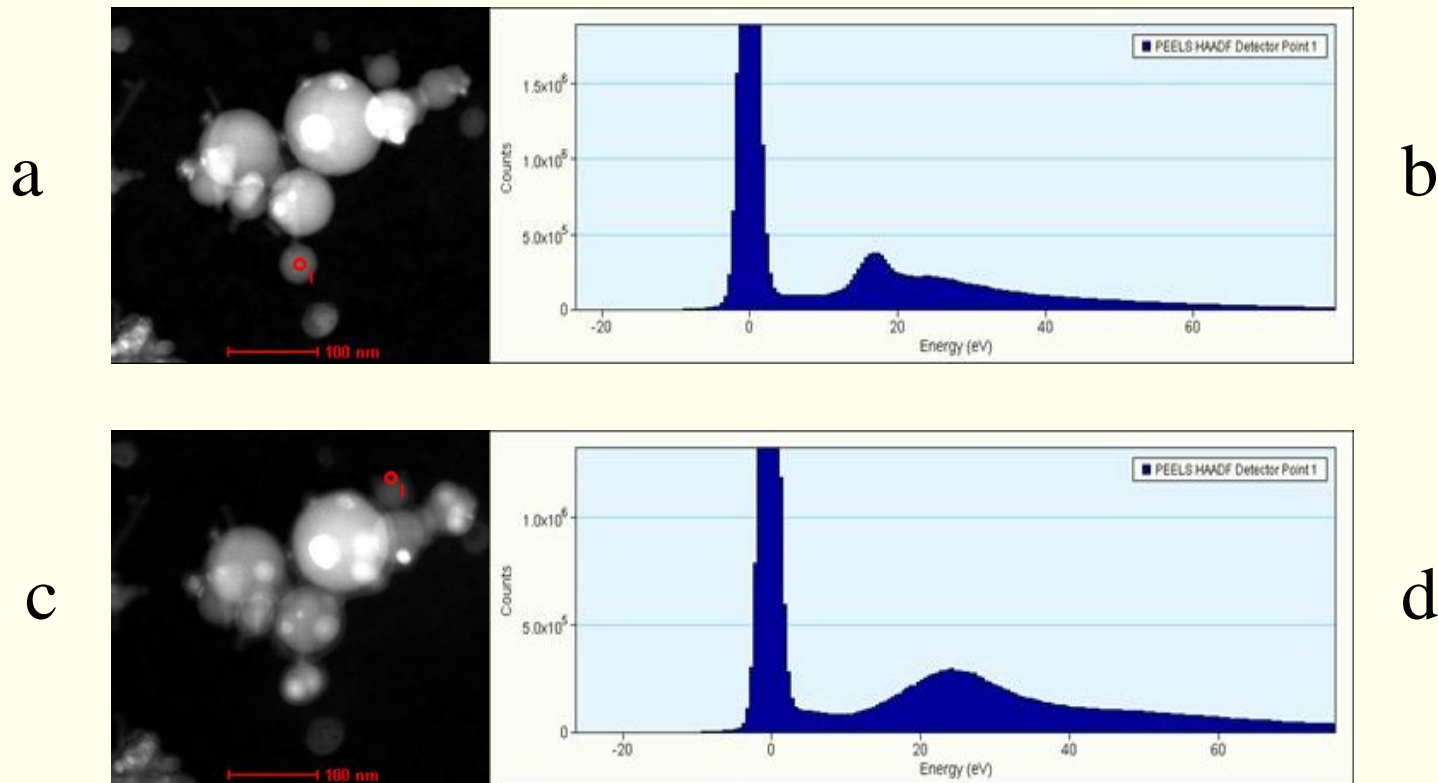
As a **case study**, nanospheres containing a crystalline silicon core covered with thin silica shell were prepared by super high-frequency plasmochemical technique and characterized in aqueous solutions by capillary zone electrophoresis (CZE).

Silica and silicon nanospheres



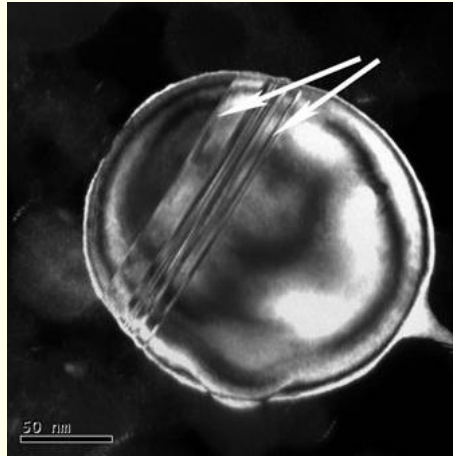
HR TEM images of the particles of silica (a) and silicon (b) samples. The insets are: on left (a) – FFT of the whole visible lattice image, on right (b) – of the rectangular area.

A crystalline silicon nanosphere



EELS spectra acquired at the center of a 35 nm particle (a-b) and at its periphery (c-d). To the left are STEM images, to the right - EELS spectra.

Crystalline silicon nanosphere - details

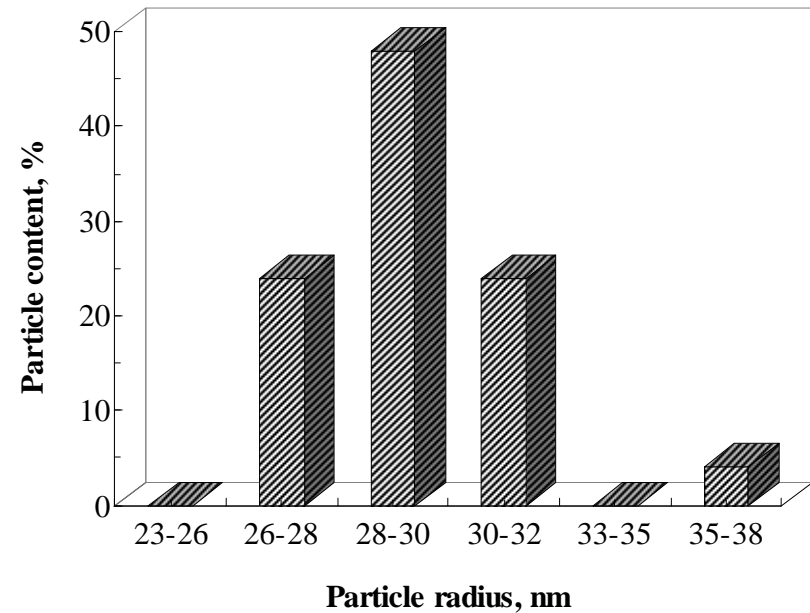
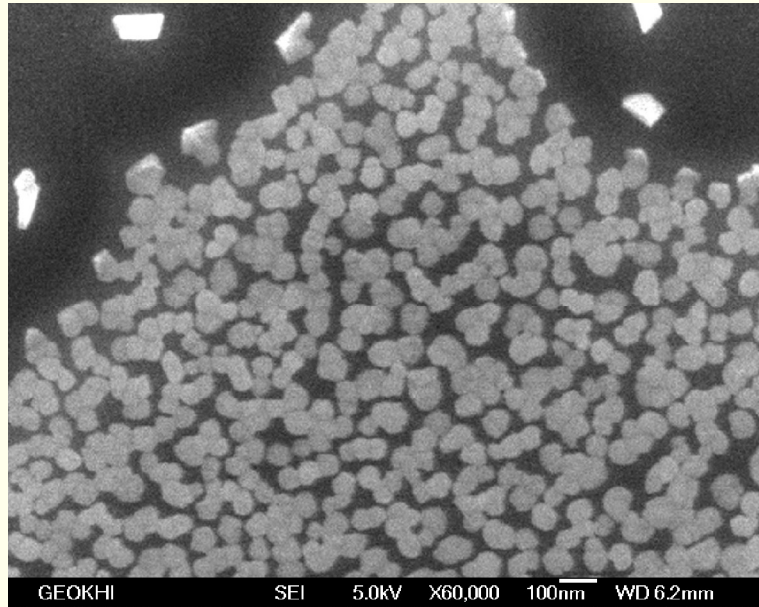


Structural defects (arrowed) and thickness variations (black & white bands) across the particle in DF TEM image.

On larger particles a silica shell reaches 2–3 nm, while on smaller particles the layer is hardly seen even using HR TEM imaging (Slide 7b) and does not exceed several Å.

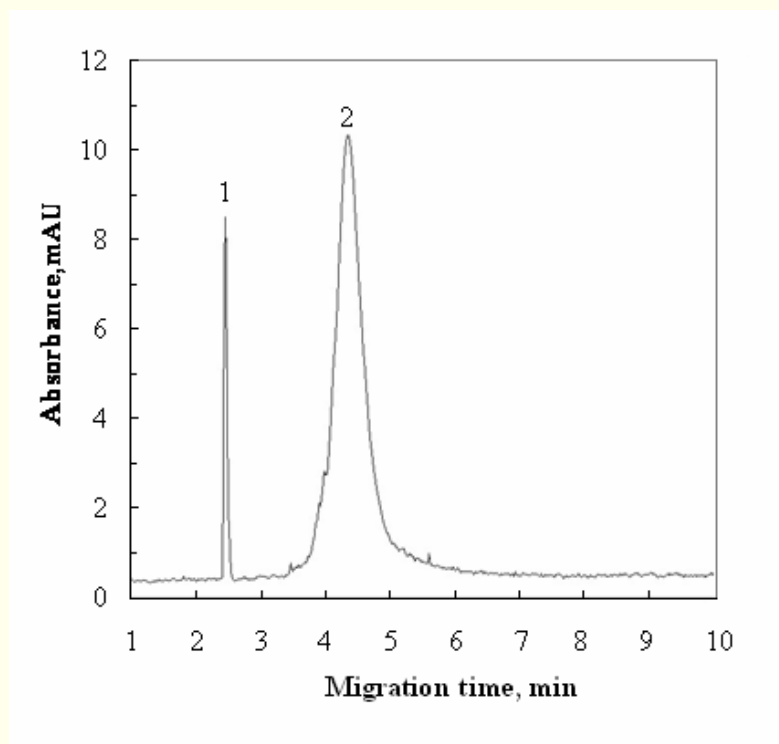
[A.Belogorokhov et al. *J. Adv. Mater.* \(2009\) 41/2:64.](#)

The particles in phosphate buffer solutions



SEM image and radius distribution of the particles freshly dispersed by ultrasonication (120 min) in the phosphate buffer solution with pH 8.5, after drying, magnification of 60,000.

Electropherogram of a fresh suspension



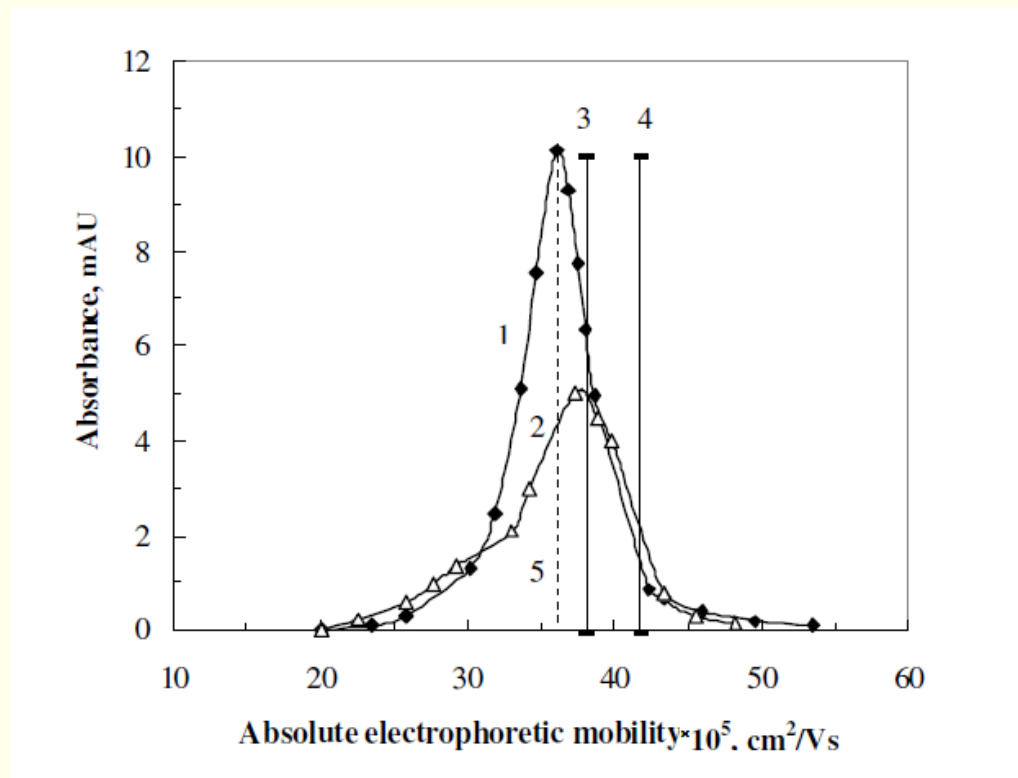
Peak 1 belongs to the EOF marker, and peak 2 - to the studied nanoparticles. The carrier electrolyte was the phosphate buffer with pH 8.5; the wavelength - 254 nm; the electric field strength - 420 V/cm.

Charge of the particles

The lowest electrolyte concentration is required to prevent nanoparticle **aggregation** and to reduce the analysis time. On the other hand, the concentration must be high enough to provide sufficient buffer capacity to maintain the pH during the electrophoretic runs. The value of 2.5 mM was chosen as a compromise.

The studied particles migrated in the direction opposite to that of EOF, when voltage is applied. Thus, the nanoparticles were **negatively** charged.

Absorbance vs absolute electrophoretic mobility



1 - freshly dispersed suspension; 2 – after 150 h storage; 3 - RM **silica** particles with av. radius of **25 nm**; 4 – the RM particles with av. radius of **50 nm**; 5 – the studied particles with the av. radius of **23 nm**. Other conditions - as in Slide 11.

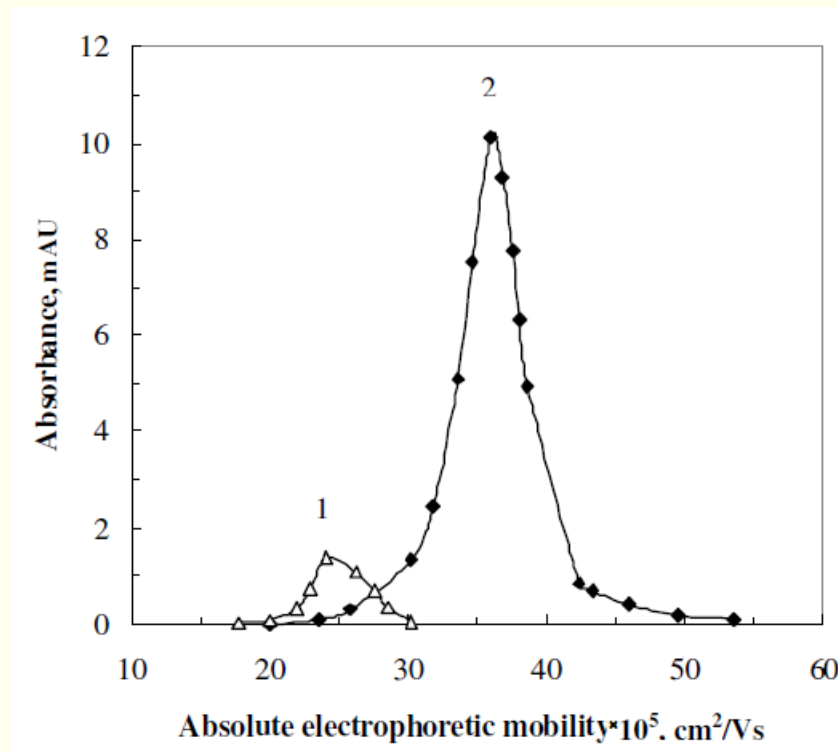
The electrophoretic mobility and z-potential

The electrophoretic mobility was calculated as $\mu_{ep} = \mu_{eo} - \mu_{app}$, where μ_{eo} is the electroosmotic mobility and μ_{app} is the apparent mobility.

Zeta potential of 58 mV was obtained for studied particles dispersed in the buffer solutions with pH 8.5. **The same** was also for the RMs with average particle radii of 25 and 50 nm (Polysciences Inc., USA) in the same buffer: 59 and 60 mV, respectively.

The similarity of zeta potential values points out the **similarity of the surface properties** of the RMs and the studied particles.

Effect of pH for the studied particles



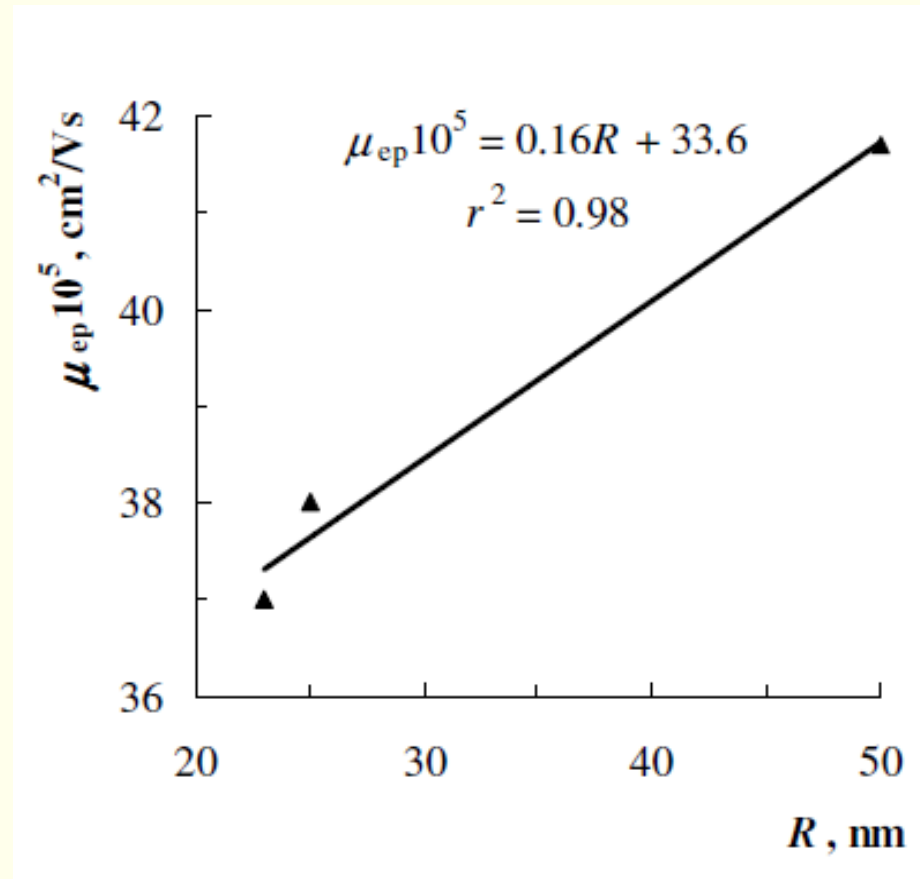
Curve 1 is for pH 5.9; curve 2 – for pH 8.5. Other conditions - as in Slide 11.

Comparison

Comparison of the curves indicates a shift of the peak towards the smaller μ_{ep} when pH value is decreased. Such a difference is caused by z-potential decreasing with reduction of the dissociation degree of acidic functional groups on the particle surface. That confirms indirectly the presence of **silanolic groups** on the surface of the particles.

The peak height reduced with decreasing pH. This alteration probably occurred due to deterioration of the suspension stability caused by decreasing the particle zeta potential. The same was observed also when ultrasonic pretreatment was more than 120 min.

Dependence of the absolute electrophoretic mobility on the particle radius



Summary: a possibility to evaluate the particle size in solutions using CZE

The dependence of electrophoretic mobility on the particle radius can be approximated by a linear regression equation with a satisfactory correlation coefficient, since the surface of both silica and silicon particles is very similar, z-potential values are practically the same, etc.

More **reference nanomaterials** are necessary for a reliable approximation, especially when an average radius of the particles under study is less than 25 nm.

N. Vanifatova et al. *Int. J. Nanoparticles* (2010) 3/1:65.

Acknowledgements

My co-authors of the cited papers: Prof. Yu.Karpov, Prof. A.Belogorokhov & Prof. Yu.Parhomenko, GIREDMET; Prof. B.Spivakov & Dr. N.Vanifatova, GEOKHI; Dr. L.Belogorokhova, Moscow State University, Moscow, Russia

Dr. I.Popov, Dr. V.Gutkin & Dr. V.Uvarov, The Hebrew University Nano-center, Jerusalem, Israel

Dr. A.Fajgelj, IAEA, Seibersdorf, Austria

Foundations: Ministry of Science of Israel & Russian Foundation for Basic Research (joint research project 3-3547 in Israel & 06-02-08226 in Russia) and Russian Academy of Sciences, Program 20.

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