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THE PREPARATION OF MULTI-ELEMENT SALT STANDARDS FOR CALIBRATION OF
EDX-SYSTEMS IN STEM USING AEROSOL TECHNIQUES

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Abstract - For calibrating an energy dispersive X-ray detecting system fitted to a STEM a set of relative peak intensities of all elements being of interest was established. For this purpose multi-element salt standards were prepared using an aerosol generating and collecting system. The calibration spectra obtained show relative values. They were converted into absolute calibration curves by comparing them with analytical values originated from measurements of one organic calibration standard of known concentration.

Introduction - Quantitative X-ray microanalysis of biological specimens in STEM needs calibration standards of known concentration for all elements being of actual interest. The most suitable standards are those which are very similar to the specimen under investigation concerning chemical composition, thickness and stability against the impact of electrons as well as against the vacuum. Organic standards like macrocyclic polyether complexes with elements uniformly distributed in epoxy resin seem to be nearest to the claimed properties (SPURR, 1). Unfortunately the preparation of those standards suffers from some limitations: (1) not each element being of interest can be incorporated in adequate concentrations without loss of homogeneity and/or polymerisation properties, (2) the preparation of such calibration standards requires a high expenditure of work. Therefore we decided to establish a set of relative peak intensities from multi-element salt standards in order to evaluate the relative sensitivity of our analytical instrumentation. These relative calibration spectra were to be established by putting the $K_\alpha$-peak = 100 and referring all other elements to $K_\alpha$. In a second step we wanted to convert these relative values into absolute ones by correlating them to analytical data from epoxid sections of known concentrations of elements, e.g. K. These standards were prepared using a modification of SPURR’s method (2). The concentrations of K were determined by atomic absorption spectrometry (2). Special attention was focussed on the fact, that the salt deposits (1) should be very small, (2) should contain several elements in equimolar concentrations, and (3) should be homogeneous. In the past several authors dealt with these problems and published their results concerning the preparation of specimens consisting of mineral salts (3, 4, 5, 6). Since they predominantly worked with electron microprobes salt particles with diameters of approximately 1 - 3 μm were accepted as being of adequate size. Homogeneity in microanalytical measurements was only achieved by analysing the specimens with a beam diameter of 10 μm (6). For analytical work with a STEM (beam diameter less than 100 nm) much smaller salt precipitates are indispensable which should be homogeneous all over their area. For this purpose aerosol generation techniques seemed to be ideal procedures to receive microdroplets of salt solutions which after draining can be collected as microprecipitates.
Materials and Methods — Analytical instrumentation: The microscope under investigation was a Hitachi H 500 transmission electron microscope equipped with a scanning device H 5010 and combined with a 145-eV-resolution lithium-drifted silicon detector (Princeton Gamma Tech) and a computer-based multichannel analyser (PGT-XCEL). The take-off angle is 68° at a distance of 13 mm. The active area of the Si(Li) crystal is 30 mm² protected by a beryllium window of 7 μm thickness.

Particle production and collection: In order to achieve a high yield of small particles, we chose the liquid dispersion method with subsequent removal of large particles. The scheme of the experimental setup is shown in Fig. 1:

Fig. 1 — Scheme of the experimental setup for particle production and collection (1 = pressure reducing valve; 2 = atomizer nozzle; 3 = feed solution; 4 = cyclone; 5 = drain solution collector; 6 = diffusion drier; 7 = silica gel; 8 = corona sampler; 9 = corona discharge electrode; 10 = collector grid)

A Schlick model 970-88 stainless steel atomizer nozzle (2) was operated with a pressure of 2.5 bar (1). The feed solutions (3) were sucked into the high velocity air jet, where the liquid was disintegrated into droplets due to the aerodynamic shear stress in the jet. The large fraction of the primary droplets (> 1 μm) was removed by centrifugal forces in the cyclone (4) (designed by LEITH and MEHTA, 7) and drained to collector (5). To obtain the residue particles necessary for calibration, the solvent was removed in a silica gel bed (7) of a diffusion drier (6), where the water molecules diffuse to the silica whereas the salt residue particles, due to their much smaller diffusion coefficient, remain airborne. These particles are about one order of magnitude smaller than the primary droplets. Most of them will be deposited in a corona sampler (8), which consists of a sharp needle (9) (as discharge electrode) connected with a negative high voltage supply of about 6 kV. Opposite to the needle, the carbon-shadowed Formvar-coated collector grid (10) was at ground potential, attached with conducting glue to facilitate deposition of the charged salt particles. The distance between the needle tip and the collector was 1 mm.

Preparation of the standard salt solutions: The following salts were used either separately or combined in salt mixtures: (a) hydrochloric acid salts of Na and K; (b) sulfuric acid salts of Na, Mg, K, Ca, Mn, Fe, Co and Ni; (c) nitric acid salts of Mg, Ca, Mn, Fe, Co and Ni; (d) KH₂PO₄. All salts were of analytical grade. They were dissolved in deionized water to obtain a final molarity of 0.1 or 0.05, respectively, for each constituent. All weighings were performed on a Mettler B6 balance with a readability of 0.5 mg.

Analytical operations: The microanalytical data were recorded by spot analysis using an accelerating voltage of 75 kV. In STEM the beam diameter was less than 100 nm (evaluated by measuring contamination lines). The beam current was 25 μA. The counting time was 200 s (“live”). Background was subtracted from the spectra manually. The analytical data used for further calculations were the net peak
integrals falling into the energy windows of 1.2 times the full width at half maximum. The numerical basis data for the correction factors of Tab. 1 are ratios of net peak integrals of the analysed elements to the net peak integral of the potassium-(Kα)-energy window (= 1). They were calculated by the multichannel analyzer.

Results and discussion — Fig. 2 shows a representative TEM-micrograph of salt precipitates. The shapes of the collected particles are nearly circular. The size distribution (Fig. 3) ranges from 30 to 350 nm with a significant accumulation of 30 to 100 nm particles (> 50%). The mean diameter is 130 nm, the median comes to 110 nm. According to the actual experimental conditions the smallest primary droplets (before draining) should be of about 100 nm (evaluated by an independent calibration of the aerosol generator). Thus the smallest particles should contain $6 \cdot 10^4$ salt molecules. Assuming statistical fluctuations in the salt concentration of the feed solution, the composition of even the finest droplets is defined within a relative standard deviation of about $4 \cdot 10^{-3}$, which is certainly negligible compared to the instrumental limitations. In fact the microanalysis of 10 small salt particles (< 100 nm) originated from 11 single-salt solutions shows maximum percentage errors of 1 - 2% concerning the ratio of cations to anions.
Encouraged by these findings precipitates of two multi-element salt solutions were analysed: (1) solution A containing MgSO₄, MnSO₄, CoSO₄, NiSO₄, and KCl; (2) solution B containing NaCl and KH₂PO₄. So two partial energy spectra appeared, which can be correlated by scaling the potassium peak being in common in both spectra. In this example, the sulfur peak is highly accumulated due to the presence of several salts of the sulfuric acid. This peak was eliminated by peak subtraction. The partial spectra were then written subsequently using an X-Y plotter. The shape of the relative sensitivity curve overlaying the tops of the peaks (Fig. 4) fits in a good way the relative peak intensity curves established by control measuring of adequate single-salt precipitates. In addition, it looks similar to those curves which are published by CHANDLER (5) who analysed single-salt specimens and MORGAN et al. (4) measuring multi-element standards, too.

In Tab. 1 the net peak integral values were taken to calculate correction factors which can be used in connection with a calibration curve of one element being incorporated in epoxid resin at a known concentration in order to evaluate the absolute concentration of all elements listed there. The advantage of the aerosol technique seems to be the possibility of producing multi-element standards consisting of homogeneous salt particles which — due to their smallness and thinness — are similar to common specimens for TEM and STEM. By varying the molar concentrations of the feed solutions the size of the particles can further be influenced. In addition, the precipitated particles seem to be amorphous (in TEM neither interference contrast was observed nor electron diffraction pattern appeared, not even after a storage period of some weeks). That means one has not to expect a dissociation of the elements within a particle due to crystallization and/or recrystallization. This need not be true for standards consisting of nitric acid salts caused by their high hygroscopicity.

**Literature**
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