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AN ANALYSIS OF THE ELEMENTAL COMPOSITION OF MICRO-SAMPLES USING EDS TECHNIQUE

ANALIZA SKŁADU PIERWIASTKOWEGO W MIKROOBSZARZE PRZY UŻYCIU TECHNIKI EDS

Abstract

A classic example of the application of electron-dispersive spectroscopy (EDS) is the observation of the microstructure of solid samples using scanning electron microscope (SEM). This provides the possibility of taking measurements of chemical composition in very small areas. Measurements can be performed on any bulk sample through adjusting the X-ray excitation parameters to the elements of its expected composition. Examples of the applications of the EDS technique in the context of environmental engineering have been presented.

Keywords: scanning electron microscope, X-ray emission, energy dispersive spectrometer, characteristic spectrum, detection limits

Streszczenie

Obserwacje mikrostruktury litych próbek przy użyciu skaningowego mikroskopu elektronowego (SEM) z możliwością wykonania lokalnego pomiaru składu chemicznego w bardzo małym obszarze, to klasyczny przykład zastosowania spektroskopii dyspersji energii (EDS). Pomiar wykonywany jest na dowolnej próbce stałej, stosując parametry wzbudzenia promieniowania rentgenowskiego adekwatne do pierwiastków, spodziewanych w składzie próbki. Omówiono przykłady zastosowania techniki EDS w zagadnieniach związanych z inżynierią środowiska.

Słowa kluczowe: elektronowy mikroskop skaningowy, emisja promieni X, spektrometr dyspersji energii, widmo charakterystyczne, granica wykrywalności

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1. Introduction

Energy dispersive spectroscopy (EDS) is a micro-analytical technique conventionally used in scanning electron microscopy (SEM) for the local determination of chemical elements in solid samples [1–3]. The sample is made from a solid material, stable in a vacuum of up to 1.5×10^{-3} Pa. The sample is then bombarded with electrons with energy levels of up to 30 keV. Another requirement for SEM is that the sample under investigation should fit dimensionally to the specimen chamber of the microscope. Samples are placed in a special holder with the surface to be subjected to analysis facing upwards [3].

Using the EDS method, the chemical composition of small objects is measured by placing the material in the vacuum chamber where it is illuminated with a focused electron beam from above. Electrons bombarding the specimen surface are scattered into the material and may ionize the specimen atoms by knocking out secondary electrons from the stationary shells. The resulting gaps in the electron shell are filled by an avalanche of electrons from the outer shells of the atom. The ionized atoms emit X-ray quanta of discrete energy, which are characteristic of the chemical elements of the material under investigation. The photons from the X-ray emission are collected by an EDS detector placed near the sample and transmitted through an electronic system to the multi-channel analyzer, in which the pulses are separated according to their amplitude. The number of quanta (the intensity) of characteristic X-rays emitted in a given time interval by the atoms of the investigated element is proportional to the concentration of that element in the sample. The complete energy-dispersive spectra are transferred to the dedicated computer equipped with a special software system for the collection, observation, calculation and storage of the spectral data.

The EDS microanalysis is regarded as a non-destructive technique because the specimen prior to analysis does not differ from the specimen after the analysis [4]. The aim of this paper is to demonstrate the effectiveness of the EDS method in material investigations performed by means of conventional SEM.

2. A brief description of the EDS technique

A single EDS measurement means the acquisition of an energy-dispersive spectrum in which (at discrete energies) the characteristic peaks of the chemical constituents are present. To determine the element concentration from the peaks obtained, it is necessary to process the spectrum (Fig. 1) [5]. The main outcome from the measurement is the value of the relative intensity of the spectral lines (*K-ratio*) measured after the optimization of the shape of the peaks (Fig. 1, pp. 3–6). The concentration of the *i*-th element in the specimen is calculated from the equation [1]:

$$\frac{C_i}{C_{(i)}} = \text{ZAF} \cdot \frac{I_i}{I_{(i)}} = \text{ZAF} \cdot K - \text{ratio} \quad (1)$$

where:

- $C_i/C_{(i)}$ – relative concentration of the element in specimen and in standard;
- $I_i/I_{(i)}$ – relative intensity of spectral lines (equal to *K-ratio*);
- ZAF – correction factor for quantitative determination of the *i*-th element.

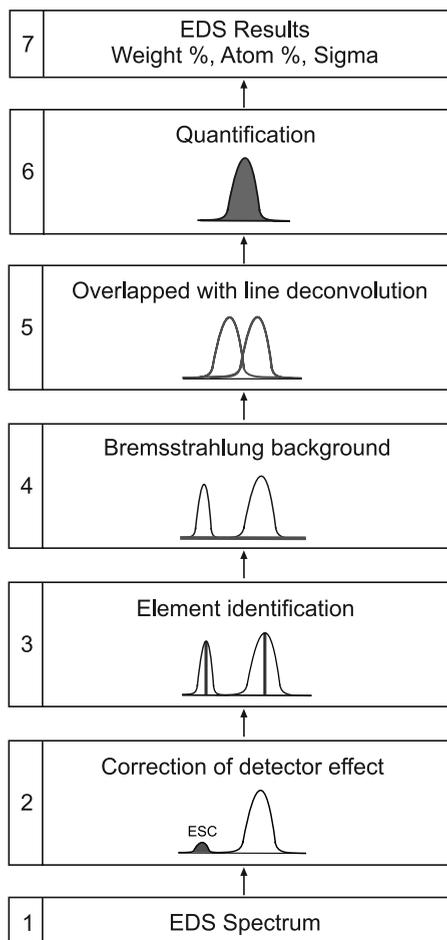


Fig. 1. Flowchart of the modeling of the emission spectrum [5]

The description of the quantitative EDS microanalysis technique is given in detail in several monographs [1, 5, 6]. Kalner and Zilberman [6] give a variety of parameter tables for the correction of ZAF and the *K-ratio*, useful for the manual calculation of element concentrations in the studies of metals and alloys. This procedure should be understandable in the absence of a fully automated system or if there is lack in confidence in the interpretation of the microanalysis results obtained from computer calculations. Currently, the entire analysis of the EDS spectrum, consisting of the qualitative identification of peaks and the calculation of the concentration of the constituent elements, is performed automatically within a minute. The proper implementation of the measurement of the spectrum requires advance planning of the experiment and a skilled operator of the microscope. In the work of Szummer [5], the corresponding algorithms (Fig. 1) implemented in the software instrumentation of modern EDS spectrometers are obtained in detail.

2.1. Electron-beam instrumentation

The most important part of SEM is the vacuum column that contains an electron gun with the applied accelerating voltage and an electron optical system, focusing the electron beam on the specimen surface.

Figure 2 illustrates the scattering paths of electrons in the material (of density ρ and atomic number Z) for different electron beam accelerating voltages (in kV). The drawing is the result of the Monte Carlo simulation of the electron scattering phenomena in a homogeneous material [1]. Since the signal of the image in SEM is gathered point by point during the scanning of the beam over the surface of the specimen, the diameter of the electron beam determines the resolution of the scanning images. And so, at a voltage of 30 kV and a beam emission from a tungsten cathode, the minimum beam diameter is about 10 nm (0.01 μm) [7]. A narrow diameter of the beam is possible (for example, on a single nanoparticle), but this is contrary to the requirement of the maximum beam current for optimal sensitivity of EDS microanalysis. The beam current increases with the beam diameter. For the qualitative analysis of elemental composition, the optimum beam diameter is from 0.1 to 1 μm , and for quantitative analysis, diameters of up to 5 μm are recommended [7]. These values are correlated with the spatial resolution of the characteristic X-ray emission from the specimen.

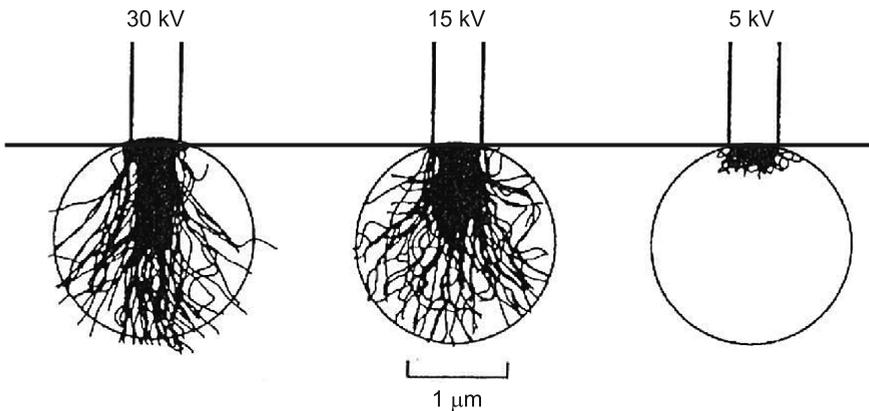


Fig. 2. Depth of beam penetration into the material at different accelerating voltages [1]

To obtain high levels of radiation characteristic of the sample at the optimum ratio of peak to background (Fig. 1, pp. 3 and 4), the energy of electrons bombarding the specimen must exceed double the *ionization potential* of the atoms in the specimen [5, 7]. Thus, for samples of unknown composition, only the first measurement of the spectrum beam voltage of 25 kV [7] will allow the recording of the emission lines of the EDS spectrum for energy up to 10 keV.

The primary electron *penetration depth* (Fig. 2) depends on the energy and density of the material. For example, the electron scattering area at 30 kV for a specimen of iron ($\rho = 7.874\text{g/cm}^3$, $Z = 26$) reaches a depth of 3.1 μm , and at 5 kV – a depth of 0.16 μm . SEM is capable of generating beam voltages of values from 0.3 kV to 30 kV. The Monte Carlo

simulation indicates that the X-ray *emitting region* is in the order of 2–5 μm , which means that the micro-volume of the analyzed specimen is derived only from the subsurface layers of the material [7].

2.2. X-rays emission

The Bohr model of the atom shows the atoms of chemical elements as a quantized system which can exchange energy only in portions of the permitted amount. The name of the series of emission in the EDS spectra corresponds to the sign of the atomic inner shell, from which accelerated electrons of the primary beam strike away stationary electrons (Fig. 3). The excitation energy levels of the L and M lines are lower than for the K series (E_M max. ~ 3 keV), hence the introduction of the electron holes in the K shell simultaneously precipitates the emissions from lines K_α , K_β and K_γ [5]. The probability of each transition is different, which results in the individual lines measured having different intensities. Spectral lines marked K_α are the strongest, thus the quantitative EDS spectrum analysis is carried out conventionally using the K series. The energy of the characteristic X-ray emission of the K series ranges from 0.185 keV for boron ^5B to tens of kilo-electron-volts for heavy elements [4].

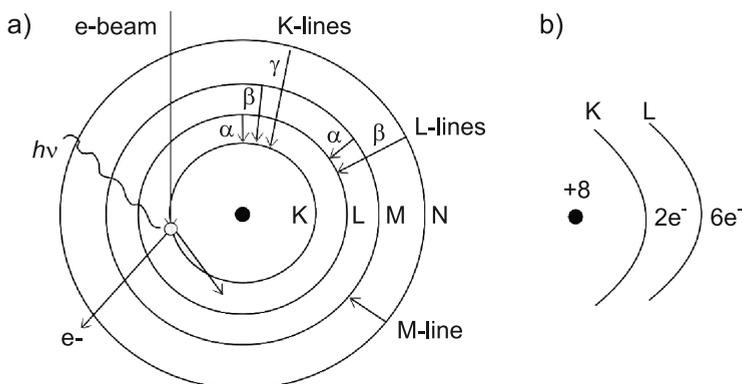


Fig. 3. Model of the atom: a) spectral lines designation; b) oxygen atom (O^8) [5]

One can see from this that the analysis of heavier elements must be carried out after the L series, as the K series of the spectrum will not be excited at the maximum SEM beam voltage of 30 kV; e.g. for uranium ^{92}U : $E_{K\alpha} = 98.43$ keV, $E_{L\alpha} = 13.61$ keV and $E_{M\alpha} = 3.17$ keV.

The full range of the characteristic radiation energy of elements (from 0.120 keV to 120 keV) is due to the conversion of wavelength ($\lambda = 0.1 \text{ \AA} - 100 \text{ \AA}$) to photon energies of electromagnetic X-radiation by the well-known equation [1]:

$$E = hc / \lambda e = 12.396 / \lambda \quad (2)$$

where:

- c – light velocity in vacuum (3×10^8 m/s);
- h – Planck's constant (6.62×10^{-34} J·s);
- e – electron charge (-1.6×10^{-19} C).

The system of spectral lines is unique and characteristic for each element and therefore, can be used to study the chemical composition of micro-samples. It should be noted that the atoms from ${}^5\text{B}$ to ${}^{10}\text{Ne}$ have only two shells filled with electrons (Fig. 3b), i.e. emissions only from the K series. The excitation energy of the K series for the light elements is very small (max. 1 keV), i.e. all peaks are gathered in the low resolution portion of the spectrum, where peaks from ${}^{11}\text{Na}$ and upward (for L series) and from ${}^{39}\text{Y}$ and upward (for M series) are imposed. Determination of the percentage concentration of light elements by EDS is also troublesome because of the intense absorption of X-ray emission inside the sample, and thereby, the ZAF correction factor is much larger than one.

2.3. Features of an EDS detector

A standard EDS detector exhibits the highest detection efficiency for K_{α} lines with an approximate energy range from 3 keV to 20 keV. The emission quanta of lower energies are absorbed by the detector window, whereas the high-energy emissions pass without registration, which is reflected in the so-called ‘escape peaks’ (ESP) (see Fig. 1, p. 2). The measurement error of ESP does not usually exceed 10%.

The main element of an EDS detector is a single crystal silicon wafer, doped with lithium ions (Fig. 4) [6]. The detector is placed between two electrodes, to which is applied a voltage of opposite signs. Under the influence of the electric field of the p - n transition, lithium ions in the detector Si(Li) diffuse into the crystal surface (thus called a silicon drift detector) [6]. When penetrating into the detector, the X-ray photons produce electron-hole pairs by ionization a silicon wafer. To create a pair of carriers in a silicon crystal, an average photon energy level of only 3.5eV is required; hence, the semiconductor detector is highly sensitive and accurate in the registration of X-ray energy impulses. The total charge produced by a single photon is integrated over the electrodes and passed on through the electronics of the spectrometer to the computer.

The Si(Li) detector’s resolving power is limited by the background residual currents induced by the Compton scattering to around 135–150 eV. Thermally induced transitions of electrons into the conduction band of the Si(Li) crystal can cover the maxima of quanta absorption, caused by the photo-electric effect. To reduce this effect, the crystal detector is placed in a tank of liquid nitrogen and continuously cooled to a temperature of -196°C .

The EDS detector is located close to the specimen surface and therefore captures the X-ray photons of different energies at the same time, which results in a high

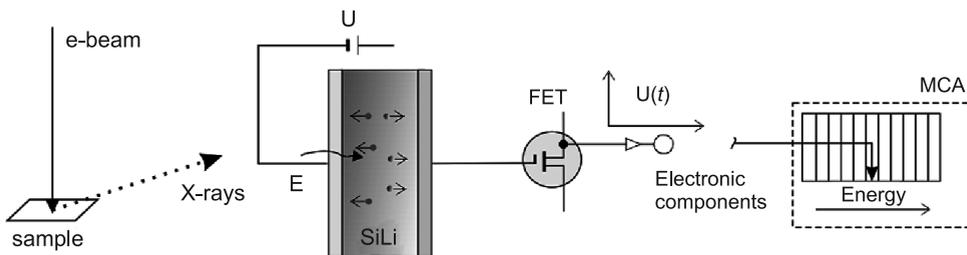


Fig. 4. Principle of the energy dispersive spectrometer with Si(Li) crystal [6]

counting rate. The counting of X-ray quanta could be described as the Poisson's process, wherein, the peak intensity measurement accuracy depends only on the total time of the measurement [4]. The typical time sufficient to collect an EDS spectrum ranges from 10 s to 100 s [7]. In practice, time restrictions are important because of the increasing contamination of the specimen. During electron bombardment, carbon, which is a product of the polymerization of hydrocarbons transmitted from the oil-rotary pump to the vacuum column, is deposited in the area under analysis.

3. Experimental examples

The study was performed with scanning electron microscopy (SEM) using the HITACHI S-3400N variable-pressure electron microscope with a tungsten filament, equipped with the *ThermoScientific*® EDS detector and the *Noran System 7* (NSS) analytical software.

Before placing the sample into the microscope, it must be thoroughly cleared of dirt adhered to the surface, and if the material is non-conductive – the entire surface must be coated with a transparent thin layer of gold or carbon. It is not recommended to investigate rusted, etched, porous or rough specimens using SEM, due to the possible distortion of the EDS analytic results. Reliable results can be obtained by preparing a flat and smooth specimen surface that is perpendicular to primary-electron beam by means of, for example, metallographic methods [3]. The test specimen can be observed in a wide range of magnifications, from about $10\times$ to $100.000\times$, using the detection of scattered electrons (SE or BSE). The working distance (WD) has to be set to about 10 mm. The transition to the EDS spectrum detection mode occurs when an electron beam is either stationary or scanning. *Secondary electrons* (SE) detectors are used for topographic imaging of the surface and *backscattered electrons* (BSE) detectors, for Z-contrast imaging.

An important condition for realization of the measurement of the spectrum is the beam current stability [18], which should be guaranteed for about four hours of tungsten filament heating. Prior to analysis, the system requires the establishment of a database (project name), cooling of the EDS detector and determination of microscope settings, i.e. the accelerating voltage, the beam current, the image magnification and the WD. After correct positioning the electron beam and the activation of the measuring equipment, the energy dispersion spectrum of the all elements present in the test microprobe is accumulated in the system memory and is displayed on the computer monitor.

The NSS system automatically identifies peaks, scanning through all elements of the periodic table, with the exception of the peaks selected 'off' manually or automatically (without the first four [19]: hydrogen, helium, lithium and beryllium). The EDS spectrum consists of a relatively small number of lines – this makes a qualitative spectral analysis sufficiently fast and accurate. The chemical composition of the investigated samples is determined using standardless analytical algorithms, where the element concentrations are normalized to 100%. The components of ZAF provide intensity correction due to the impact of X-ray emission on the sample materials excitation (Z), the probability of absorption (A), and secondary fluorescence (F) at a constant angular set of the detector relative to the specimen.

3.1. Standardless semi-quantitative analysis

The point analysis of the elemental composition was performed with the electron beam at a fixed position. An example of standard EDS analysis was shown for a steel mesh taken from a mechanical water filter used in domestic installations (Fig. 5). Such a filter retains solid particles, such as sand and rust. Unlike other filters tested, on which white-yellow precipitates appear, in this instance, no pollution could be observed with the naked eye. At relatively low magnifications, the images in the detection of secondary electrons (SE) exhibit an excellent depth of field. One can show the weave mesh and measure the thickness of the wire (which has an estimated thickness of about 250 μm) using an automatic zoom scale, shown in the menu bar of the image.

The mesh was oriented in such a way as to focus the electron beam in the center of a cross-section of the cut wire (Fig. 5). Electron beam accelerating voltage was 15 kV and the counting time of the spectrum was 30 s.

Figure 6 shows the dispersion of the energy spectrum of X-rays from the selected point (micro-area) of the sample. Distinct characteristic peaks of K_{α} and L series for iron ^{26}Fe , chromium ^{24}Cr and nickel ^{28}Ni are clear for specialists that the material investigated is a stainless steel [8]. Precision of measurement is increased by the procedures for the automatic search of peaks (Fig. 1, p. 3). For example, Figure 6 includes both the emission intensity and the theoretical position of the chromium spectral lines which are saved in the analytical data base of the EDS spectrometer. However, the accuracy of quantitative analysis depends on systematic errors of the spectral modeling (Fig. 1) entering the final results. Before calculations of the ZAF, correction of equation (1) is needed, both the position and width of each peak undergo rigorous mathematical analysis, such as deconvolution of the Gaussian curve (Fig. 1, pp. 5 and 6). Results of the concentration measurement of the elements are presented in tabular form (Tab. 1). The list of the analyzed elements is created automatically on the basis of all the peaks labeled as ‘identified’ by the NSS, or labeled manually (e.g. selecting the option ‘peak-off’ of carbon).

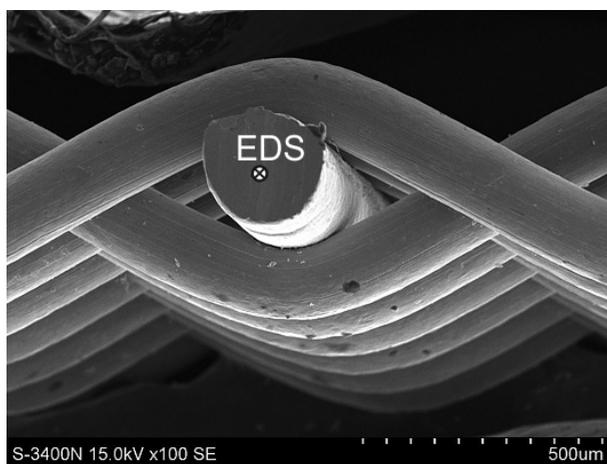


Fig. 5. Wire cross-section with selected point of spectral analysis, 100 \times

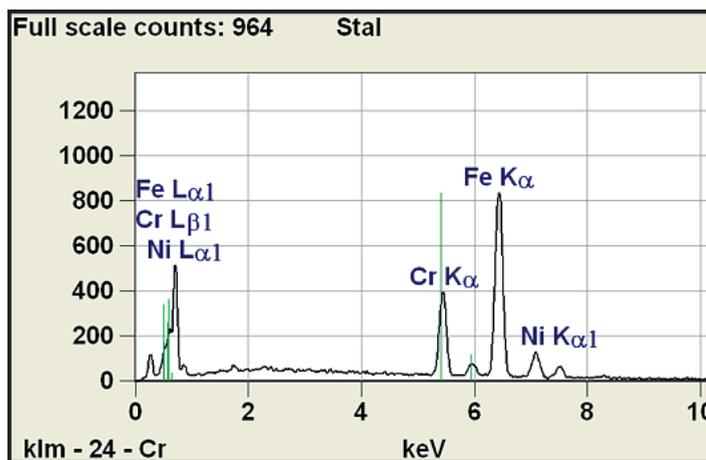


Fig. 6. Energy dispersive spectrum of stainless steel (experimental)

Table 1

Results of EDS analysis of stainless steel investigated

Element	K-Ratio	Z	A	F	ZAF	Wt. %	Wt. % Error	Atom %
Fe K	0.71	1.002	1.019	0.992	1.012	72.54	+/- 1.11	71.86
Cr K	0.21	0.999	1.006	0.879	0.884	18.59	+/- 0.44	19.78
Ni K	0.08	0.990	1.065	1.000	1.054	8.87	+/- 0.96	8.36
Total						100.00		100.00

A standardless EDS analysis of the chemical elements in the filter mesh showed that it is made of stainless steel type AISI 304, formerly called 18/8 (containing 18 wt.% Cr and 8 wt.% Ni). This steel is widely used, it is an austenitic stainless steel, resistant to electrochemical corrosion, it is strong, ductile and weldable and has a reduced content of carbon up to 0.03% C [8].

3.2. Chemical calculations based on stoichiometry

The EDS qualitative analysis can be performed with an electron scanning beam. The smaller the surface area of a scanning beam, the larger the specimen image magnification. Figure 7 shows the cross-section of the layer of *Zinalium*[®] with a thickness of about 70 μm [9], applied for external protection against the corrosion of buried ductile iron pipes. It has been observed from systematic microscopic studies of pipe sections that a zinc base coating is separated from the ductile iron substrate by a layer of iron oxide with a thickness of approximately 60–80 μm [10, 11]. The aim of the EDS analysis was to investigate the origin of the scale. Approximately 500–700 times magnification is the minimum required to distinguish the different structural layers in the specimen.

To be able to center the beam carefully within the analyzed micro-region, very careful preparation of the metallographic micro-section is required for the quantitative analysis of structurally heterogeneous materials. Errors in the measurement of the intensity of the spectrum, caused by any unevenness of the specimen surface, would be difficult to estimate. For example, the surface convexity of $0.1\ \mu\text{m}$ can reduce the value of the measured intensity by 5–7% (due to local absorption increase, thus the ZAF correction) [6]. Therefore, any analysis of a single point EDS measurement may not be representative of the entire specimen.

EDS spectra were collected from different locations on a homogeneous specimen, where each single scan area was $10 \times 10\ \mu\text{m}^2$. Analyzed areas are marked much darker in the SE image (Fig. 7), because the increase of the spectrum recording time under a focused beam leads to carbon layer deposition. When considering the spatial resolution of X-ray

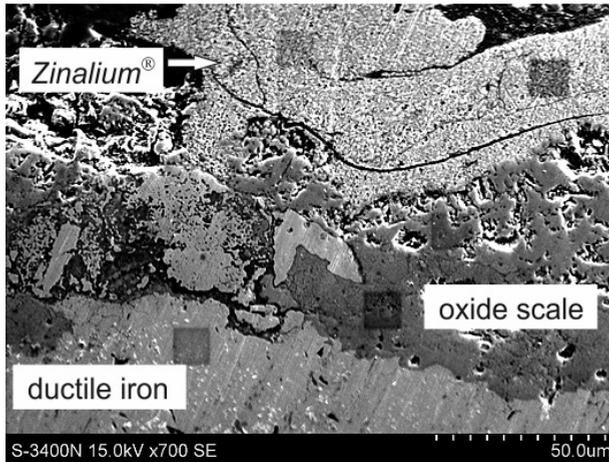


Fig. 7. Cross-section of the coating and carbon-contaminated areas of microanalysis, 700×

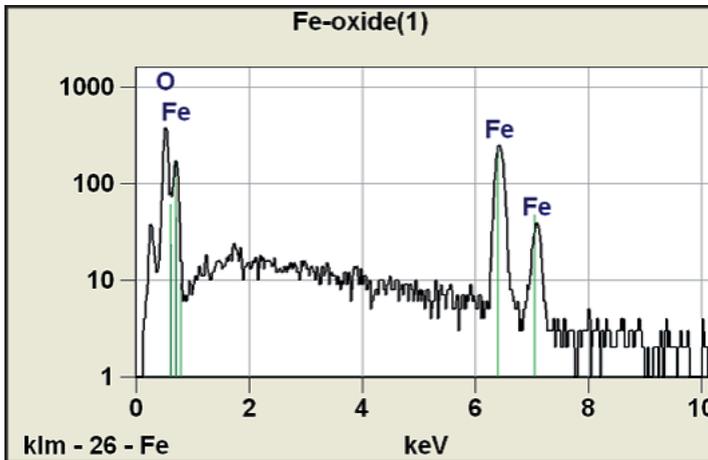


Fig. 8. Energy dispersive spectrum of the sub-coating oxide scale (logarithmic)

emissions, the inelastic electron scattering zone should be considered (Fig. 2) to ensure, that the analyzed micro-area does not extend to the border of two different microstructure components. The spectrum in Figure 8 (in logarithmic intensity scale) comes from a homogeneous area of the sub-coating oxides. The peak from carbon at 0.28 keV was excluded from the analysis because it was not representative for the specimen. Table 2 shows that the iron is combined with oxygen in the ratio of 7:3. Using simple chemical formulas (the atomic weights of elements in one molecule of iron oxide) [12], the Fe_2O_3 compound was identified. The actual standards [13] do not require the removal of the oxide layer, which is a product of the heat treatment of the ductile iron castings, on the surface of the pipes. Results from microscopy investigations of the *Zinalium*[®] coating raise question about the effectiveness of metal spraying as a means of the corrosion protection of pipes because the coarse-crystalline oxide substrate shows evidence of poor adhesion to the pipe surface [14].

Table 2

Results of EDS analysis of the undercoating oxide scale

Element	K-Ratio	Z	A	F	ZAF	Weight %	Atom %
O K	0.25	0.849	1.680	0.998	1.422	30.80	60.84
Fe K	0.75	1.092	0.996	1.000	1.088	69.20	39.16

3.3. Studies of sample homogeneity using x-ray maps¹⁾

In addition to the heterogeneity of the distribution of the microstructure components, other components can be hidden under the surface of the specimen, thus affecting the EDS result. Therefore, the quantitative analysis of the elemental composition should be preceded by studies of the homogeneity of the specimen volume analyzed. Just as scanning electron images, one could obtain pictures of the relative distribution of the concentration of chemical elements on the samples surface using the EDS technique (Fig. 9). To this end, the energy analyzer is set on a selected line of the X-ray spectra, while the scanning primary-electrons beam is synchronized with the computer speed, so this enables the imaging of the element localization on the monitor [4].

The transmitted signals form maps of the element distribution, with higher image brightness corresponding to areas of high element concentration. The mass-sensitivity of EDS analysis substantially depends on the ratio of peak signal to emission background. Obtaining maps of the element distribution is possible only for concentrations of over 1% [7] because peaks from trace elements are extremely difficult to separate from the background (Fig. 9, O-K map). For concentrations below few tenths of a percent, peak intensity is higher than the background intensity only about 30–50% [6]. Errors in the cut-off of a background level may result from the different background intensity on the left and on the right side of the peak (see Fig. 8). Therefore, for measurements of the background level, the dependency of the intensity of the continuous spectrum from

¹⁾ Elemental mapping was performed during Hitachi Workshop in the Warsaw University of Technology, October 2011.

the atomic number is usually applied [6]. Figure 9 contains an SE image of a multilayer sample (named 'Grey'), as well as the corresponding maps of the distribution of chemical elements on the scanned surface. The metal specimen surface oxidizes easily in air (before the specimen is placed in a vacuum), hence the 'noise' signals from a thin oxide layer (see O-K map). The Si-K map shows that the silicon is uniformly distributed in the ductile iron (in iron-rich area, see Fe-K map). Moreover, the epoxy layer contains large amount of Ca (see Ca-K map) and uneven Si distribution. The aluminum layer has a variable thickness of about 10 μm to 75 μm (see Al-K map).

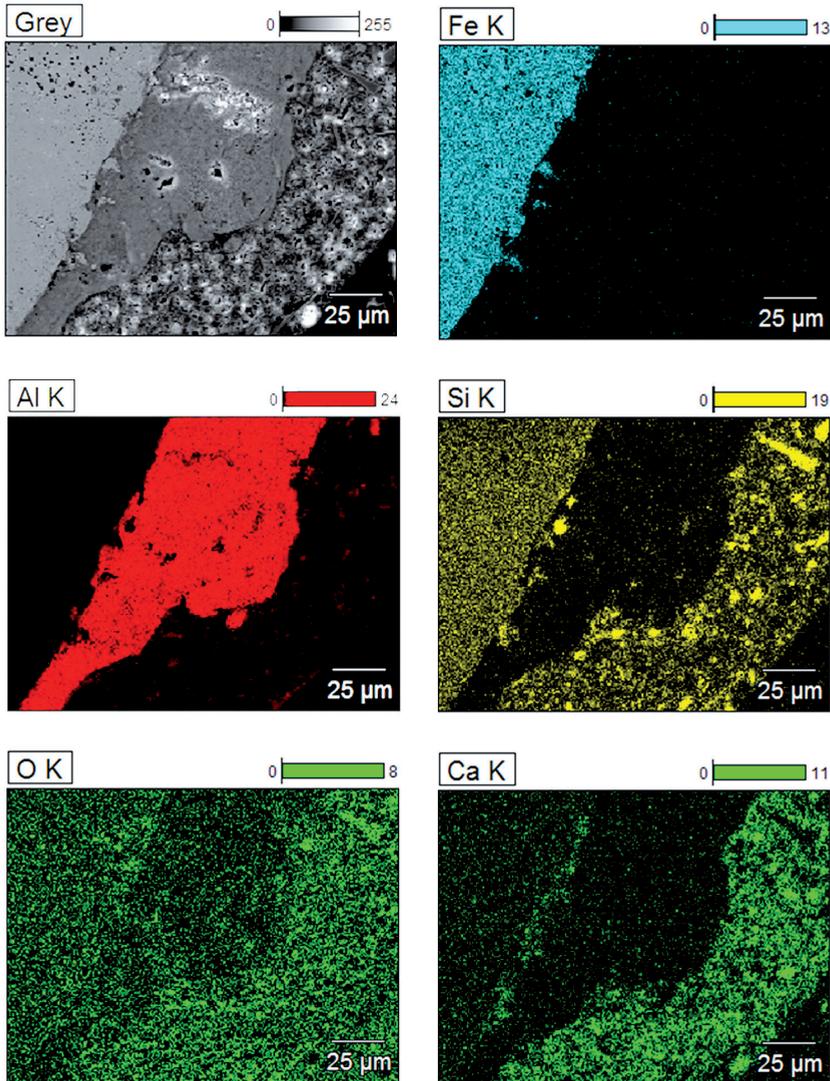


Fig. 9. Map of element distribution in cross-section of the multilayer

Because of the low spatial resolution of X-rays (emission zone of about 2–5 μm), the mapping procedures do not provide enough quantitative information, such as that obtained via point EDS analysis. However, each map can be represented in a different color, which is useful when extracting the location of an element in multi-constituent specimens (like cement mortars). Mapping¹⁾ is also used for imaging the chemical gradients on the cross-section of the specimen, such as element depth depletion far from the surface boundary.

3.4. Imaging of the atomic number distribution

Establishing of the „quasi-chemical” contrasts on the scanning images in SEM, the so-called Z-contrast, is possible by detecting the backscattered electrons from the specimen (BSE). These are electrons of the primary beam, which scatter elastically almost perpendicularly to the sample surface (no loss of kinetic energy) due to the braking force caused by the Coulomb field of the atomic nuclei. Figure 10 demonstrates the usefulness of Z-contrast for the qualitative comparison of the chemical composition of similar samples of materials.



Fig. 10. Sediments of different composition imaged in Z-contrast, 25 \times

In the BSE image, sediments taken from different measuring points (labeled as no. G1 and no. g31) have been compared. Measuring point no. G1 is located in the central part of the Reservoir Goczałkowice. The sediment is dominated by clay fraction of the soil (Fig. 11), while the concentration of iron amounts 34 mg Fe per gram of dry weight [15]. Measuring point no. g31 is located on the south-eastern side of the reservoir, in the pumping area of Frelichów, where iron is a pollutant in the natural water environment [16]. The sediment is dominated by sand fraction of the soil [15]. The iron content in that measuring point was 140 mg Fe per gram of dry weight.

The observed Z-contrast is due to the fact, that the material containing the heavier elements will scatter more BSE electrons and thus looks brighter. Therefore, the interpretation

of the BSE image is as follows: in Z-contrast, sediment no. g31 is revealed as a bright component due to the higher concentration of ^{26}Fe , because iron is an element heavier than silicon ^{14}Si , which in turn is the main component of the sediment no. G1.

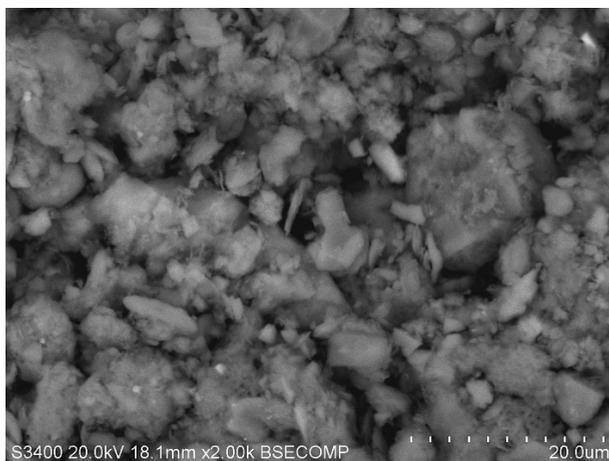


Fig. 11. Magnified image indicating the fineness of the investigated sediment, 2000×

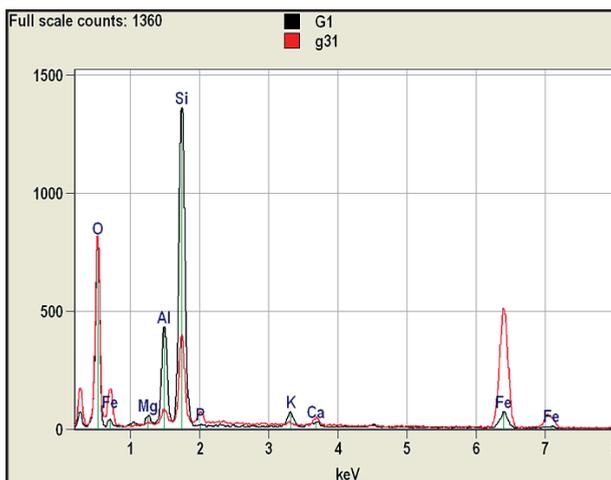


Fig. 12. Comparison of the energy dispersion spectra of two sediments

Table 3

Results of EDS analysis of the sediment samples

Specimen Nr	Chemical composition, Wt %							
	Na	Mg	Al	Si	P	K	Ca	Fe
G1	1.46	1.59	15.27	61.77	0.90	4.67	1.44	12.90
g31	0.23	0.39	2.84	15.49	2.60	0.36	1.37	77.21

The summary of the EDS spectra collected from each area separately confirms these observations (Fig. 12). The analysis was carried out over areas of around $50 \times 50 \mu\text{m}^2$ at an accelerating voltage of the beam 20 kV. Monte Carlo simulations have shown that for a primary beam energy of 20 kV, the scattering depth of the BSE electrons into a specimen reaches about $1 \mu\text{m}$ [7]. It is known that a quantitative analysis of sediments by EDS technique may not be very accurate due to the complex composition of these kinds of samples and their high fineness [1, 18]. Only chemical elements with an atomic number $Z \geq 11$ can be included into the calculations of element concentrations (Tab. 3).

For sediment no. G1, intense characteristic peaks pertaining to aluminum silicates and small quantities of iron have been recorded. Sediment no. g31 contains mainly iron-silicon, but most of the elements detected were present in trace quantities (0.2–1.0% by weight). EDS quantitative analysis may be considered only as an estimate, since the errors in the correction ZAF for any ‘powder’ specimen, even with exclusion of light elements analysis (e.g. oxygen ^{16}O), are quite large [1, 7].

4. Conclusions

More than half of the research tasks are limited to the qualitative analysis of the elemental composition of solids with the objective of answering the question of what elements are in the sample, instead of performing a quantitative analysis. The demand for quantitative EDS is high. However, most research problems require knowledge of the structure of the material and careful preparation of the EDS analysis. In general, the accuracy of calculated concentrations of individual elements is affected by the accuracy of the relative intensity of all the elements in the specimen (by adjusting ZAF). Basically, one operates a hypothetical composition of the sample, i.e. without light elements or dependence on stoichiometry, and equates results of the spectrum measurements to 100% of the total composition.

The EDS quantitative research method cannot be considered as routine like other spectroscopy-chemical methods [17]. The analysis reliability depends on the operator’s skills, the diligent execution of the experiment and the correct problem formulation. It is pertinent to note that energy dispersive spectroscopy (EDS) is effective only for a specific class of materials containing heavy elements, and in a concentration above the limit of detection [17–19]. Due to the methodological difficulties of the various stages of the quantification analysis of the chemical composition, to carry out specific measurements on a scanning electron microscope with the EDS technique, it is the equivalent of complex research work.

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