

## ANALYSIS OF IONIC IMPURITIES IN ELECTRICAL ROTATING MACHINES INSULATORS BY ANALYTICAL TECHNIQUES

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**Abstract.** *The insulation used in electrical rotating machines is a major component that influences their operation parameters. It is therefore essential to identify the methods of investigation and new technological processes to improve quality of the insulation. Traces of transition metals have been found in the insulation of cables PE. These transition metals causes degradation of insulation, affect its insulating properties and can lead to undesired electrochemical processes under the electrical stress factor. Traces of transition metals in insulator can be determined only by means of atomic and nuclear techniques of high sensitivity and precision. In this paper are presented some analytical techniques that can be used in the analysis of insulators in order to establish the most suitable method to determine the concentrations of ionic impurities. By technique Inductively Coupled Plasma Mass Spectrometry – ICP-MS, were identified and quantitative determined in insulator the following chemical elements: Cu, Pb, Zn, Cr, Cd, Al, Ni, Co, Fe and Mn.*

**Key words:** insulator, stress factor, methods, electrical rotating machines

### 1. Introduction

The insulation used in electrical rotating machines is a major component that influences their operation parameters. It is therefore essential to identify new methods of investigation and new technological processes to improve quality of the insulation. Traces of transition metals have been found in the cables insulation. These transition metals can produce degradation of highly oxidative ionic impurities in insulation and affect its insulating properties and can lead to undesired electrochemical as a electrical stress factor. Traces of metal insulator transition can only be determined by atomic and nuclear techniques of high precision and high sensitivity. Therefore it is important to make a short presentation of analytical methods for determining the most suitable technique,

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for analyzing of impurities in insulators. This study is based on development practical and different ways of implementing the methods for analysis of trace metals atoms transferred in insulation.

An analytical method applied for the determination of the trace metals in any sample is composed of the following three steps: 1. Sampling, 2. Pretreatment of sample which depends on analyte of interest and consists in acidification, acid digestion, filtration, preconcentration, etc., and 3. Analyses; using one of the next atomic and nuclear methods of high precision and sensitivity: *Atomic Absorption Spectrometry(AAS)*; *Atomic Emission Spectrometry(AES) in two variants*; Inductively Coupled Plasma – Atomic Emission Spectrometry(ICP-AES) and Inductively Coupled Plasma –Mass Spectrometry(ICP-MS); *X-ray Fluorescence (XRF)* in three variants: Energy Dispersive X- Ray Fluorescence Spectrometry (EDXRF), Wave Dispersive X- Ray Fluorescence Spectrometry(WDXRF) and Particle Induced X-Ray Emission Spectrometry (PIXE); *Particle Induced  $\gamma$  - Ray Emission (PIGE)* and *Neutron Activation Analysis (NAA)*[1-18].

Analysis technique used must meet the following conditions; high sensitivity (lower detection limit), the physical state of the sample matrix, experimental devices available and the cost for one analysis.

## **2. Description of methods for elemental analysis.**

**2.1. Atomic Absorption Spectrometry (AAS)** [1-4, 13] is a spectroanalytical method for the quantitative determination of trace elements using the absorption of optical radiation (light) by free atoms in the gaseous state. AAS can be used to determine over 70 different elements in solution or in solid samples (processed in liquid form) contained in the large spectrum of samples: environmental, metallurgical, biological, archaeological, pharmaceutical and so on. AAS is based on the exponential Lambert-Beer law. The law Lambert-Beer is rigorously respected only for a monochromatic radiation. The intensity of a beam of radiation transmitted through the atomic vapor cloud sinks decreases exponentially with the thickness of the layer of substance permeated. AAS method applies only in relative variant. It is a method of analysis monoelement. Sensitivity of the method is in the range, ppb–ppm.

**2.2. Atomic Emission Spectrometry (AES)** [2, 5, 6, 13] is applied in two variants: Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS).

**2.2.1. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)** [2, 5,6,19,20]. ICP-AES uses an inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. A plasma source is used to dissociate the sample into its

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constituent atoms or ions, exciting them to a higher energy level. They return to their ground state by emitting photons of a characteristic wavelength depending on the element present. This light is recorded by an optical spectrometer. When calibrated against standards the technique provides a quantitative analysis of the original sample. Advantages of ICP-AES are excellent limit of detection and linear dynamic range, multi-element capability, low chemical interference and a stable and reproducible signal. The detection limits for many elements are in the range of concentrations (100 ppb - 1ppb).

**2.2.2. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)** [20] is a type of mass spectrometry with which it is possible to detecting metals and several non-metals at concentrations as low as one part per billion (ppb) on non-interfered low-background isotopes. This is achieved by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions. The ICP-MS can be utilized as a quantitative tool to determine the concentration of a specific analyte, or qualitative tool to determine the metal speciation in a sample. ICP-MS has many advantages over other elemental analysis techniques, including: detection limits for most elements equal to or better than those obtained by AAS and XRF methods; the ability to handle both simple and complex matrices with a minimum of matrix interferences due to the high-temperature of the ICP source; superior detection capability to ICP-AES with the same sample throughput; the ability to obtain isotopic information.

**2.3 X-Ray Fluorescence (XRF)**[3,7-9,11-18] consist in emission of characteristic X- rays from a material that has been excited by bombarding with high-energy X-rays and accelerated charged particles (proton, alfa, heavy ions) using an accelerator. The phenomenon is widely used for elemental analysis particularly in the investigation of samples from environmental, metallic materials, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology. XRF can be applied in following experimental arrangements: Wave Dispersive X-Ray Fluorescence Spectrometry(WDXRF), Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF): - with X ray (X-ray tube) or gamma ray sources, or with accelerated charged particles (Particle Induced X-Ray Emission -PIXE).

**2.3.1. The WDXRF** [21, 22] analyzer uses a X-ray source (X ray tube) to excite a sample. X-rays that have wavelengths that are characteristic to the elements within the sample are emitted and they along with scattered source X-rays go in all directions. A crystal or other diffraction device is placed in the way of the X-rays coming off the sample. A X-ray detector is position where it can detect the X-rays that are diffracted and scattered off the crystal (Bragg law). Depending on the spacing between the atoms of the crystal lattice (diffractive device) and its angle in relation to the sample and detector, specific wavelengths directed at the

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detector can be controlled. The angle can be changed in order to measure elements sequentially, or multiple crystals and detectors may be arrayed around a sample for simultaneous analysis. Sensitivity at a lower level 1 ppm.

**2.3.2. The EDXRF**[3,7, 21] analyzer also uses an X-ray source (X-ray tube, gamma ray source to excite the sample but it may be configured in one of two ways: The first way is direct excitation where the X-ray beam is pointed directly at the sample. Filter made of various elements may be placed between the source and sample to increase the excitation of the element of interest or reduce the background in the region of interest. The second way uses a secondary target, where the source points at the target, the target element is excited and fluoresces, and then the target fluorescence is used to excite the sample. A detector is positioned to measure the fluorescent and scattered x-rays (characteristic X-ray) from the sample and a multichannel analyzer and software assigns each detector pulse an energy value thus producing a spectrum. The sensitivity is in the range 1 ppm up to 10 ppm.

**2.3.3. Particle-Induced X-Ray Emission (PIXE)**[9, 12, 14, 18] is a technique also used in the determining of the elemental concentrations from a large spectrum of materials. When a material is exposed to an ion beam (proton, alpha-particle, heavy ions) provided by an accelerator, atomic interactions occur that give of electromagnetic radiation of wavelengths in the X-ray part of the electromagnetic spectrum specific to an element. PIXE is a powerful yet non-destructive elemental analysis technique now used routinely by geologists, archaeologists, art conservators and others to help answer questions of provenance, dating and authenticity. The technique was first proposed in 1970 by Sven Johansson of Lund University, Sweden, and developed over the next years in many countries, including in Romania, at Institute for Physics and Nuclear Engineering (IFIN HH). A recent extension of PIXE using highly focused beams (down to 1  $\mu\text{m}$ ) gives the additional capability of microscopic analysis. This technique, called microPIXE, can be used to determine the distribution of trace elements in a wide range of samples. In PIXE elemental analysis method the sensitivity is in the ppm range.

**2.4. Neutron Activation Analysis (NAA)** [7, 10-12] is a sensitive multi-element analytical technique used for both qualitative and quantitative analysis of major, minor, trace and rare elements from any samples: for determining the concentrations of elements in a vast amount of materials (environmental, metallic and nonmetallic, historical artifacts, etc.). NAA method is based on neutron activation (capture neutron of nuclei) and therefore requires a source of neutrons-nuclear reactor with high neutron flux, about 10-14 n/cm<sup>2</sup>s .The sample is bombarded with neutrons, causing the elements to form radioactive isotopes. The radioactive emission and radioactive decay paths for each element are well known.

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Using this information, it is possible to study spectra of the gamma emissions of the radioactive sample, and determine the concentrations of the elements within it. NAA can also be used to determine the activity of a radioactive sample. By NAA method may be analyzed a wide spectrum of different chemical elements contained in sample: from F up to U. Over 62 chemical elements can be analyzed with NAA but is relatively expensive to be used because can be applied only at a nuclear reactor. Until the introduction of the ICP-MS and PIXE analysis techniques, NAA was the standard analytical method for performing multi-element analyses with minimum detection limits in the ppt-ppm range.

### **3. The choice of the analytical method.**

Elemental analysis methods described above are characterized by very good precision and high sensitivity which is in the range ppt-ppm.

Selecting the elemental analysis method for our researches must be done in the following conditions: high accuracy, high sensitivity, time to perform the experiment to be relatively short, relatively low cost and to have access to an experimental device of high technical performance.

In our research, to determine concentrations of metal atoms transferred in insulator we have used the Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) technique by using iCAP™ Q ICP-MS device from Multidisciplinary Research Institute for Science and Technology in Valahia University of Targoviste (VUT).

### **4. Experiment and results**

Some preliminary results obtained so far [23]. We analyzed eight samples of insulator. Insulator samples were collected after 30 days of electrical rotating machines operation.

The samples of insulator were digested on a hot plate in 10 mL (HNO<sub>3</sub> 67%, Merck) by using a TOPwave Microwave-assisted pressure digester. The digestate was filtered and diluted to established volume (i.e. 50 mL). The analysis and quantification of trace elements including Cu, Pb, Zn, Cr, Cd, Al, Ni, Co, Fe, Mn, Sr, Ba and Ag in liquid mineralized samples was performed by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) by using iCAP™ Q ICP-MS device. Measurement was performed using internal standard and 7 level calibration. Blanks were recorded for each step of the digestion and dilution procedures.

Precision of the measurements was reported as percent relative standard deviation (%RSD) for each element, which was calculated as the standard deviation divided by the average concentration. Isotopic measurements of analyzed elements using ICP-MS achieved a precision of 1-2% RSD, excepted Zn and Ba which exceed than 2% (e.g. 5% RSD for Zn and 6% RSD for Ba).

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The detection limits for each analyzed elements were: Al ( $\mu\text{g/L}$ ) < 0.5%; Cr ( $\mu\text{g/L}$ ) < 0.2%; Mn ( $\mu\text{g/L}$ ) < 0.2%; Fe ( $\mu\text{g/L}$ ) < 1.0%; Co ( $\mu\text{g/L}$ ) < 0.1%; Ni ( $\mu\text{g/L}$ ) < 0.1%; Cu ( $\mu\text{g/L}$ ) < 0.2%; Zn ( $\mu\text{g/L}$ ) < 0.5%; Sr ( $\mu\text{g/L}$ ) < 0.2%; Ag ( $\mu\text{g/L}$ ) < 0.1%; Cd ( $\mu\text{g/L}$ ) < 0.1%; Ba ( $\mu\text{g/L}$ ) < 0.2%; Pb ( $\mu\text{g/L}$ ) < 0.1%.

The experimental concentration values (in ppb) of metallic elements impurities in insulator samples obtained by ICP-MS analysis are given in figs. 1a, b, c.

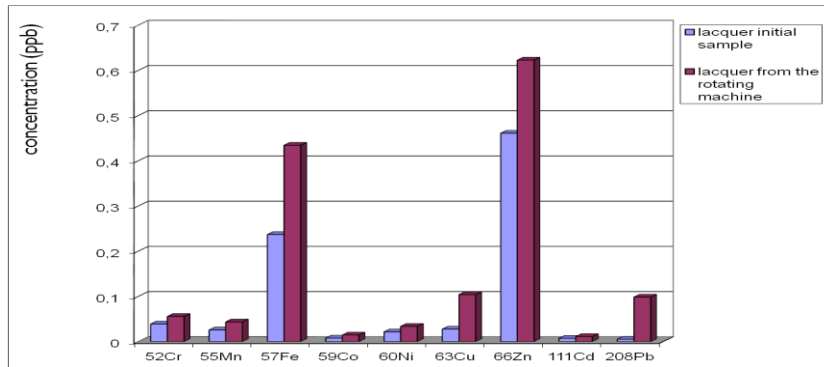


Fig. 1a.

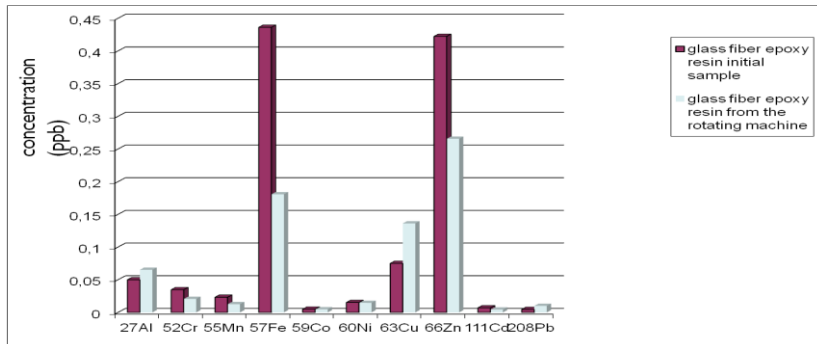


Fig 1b.

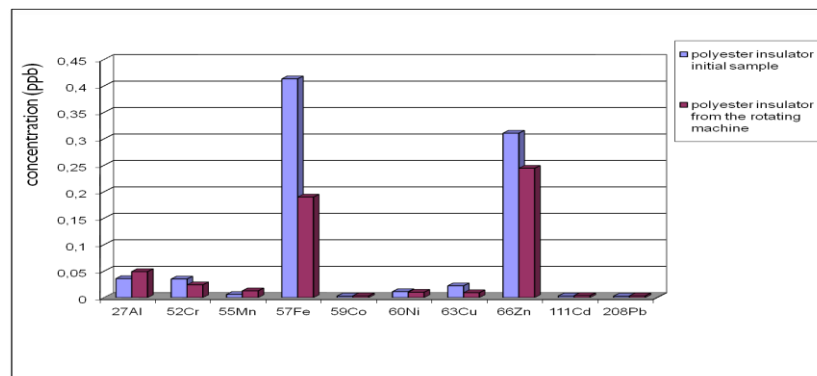


Fig.1c.

## 5. Comments

- With the ICP-MS technique we can detect small modifications of concentration of metals in the insulator. Thus is possible to imagine a mechanism for the electromigration in the insulator.
- The concentrations of iron, copper, zinc and lead are the ones that vary the most in the insulating lacquer.
- The noticeable differences in concentration in the glass fiber epoxy resin insulator appear at iron, copper and zinc.
- The polyester insulator has major changes in the concentrations of iron and zinc.
- These results suggests that the electromigration process, which is a long-term process, starts by transferring metallic ions between the conductor and insulator as a starting phase.

*Acknowledgements.* The work was presented at the Scientific Session of AOSR, Iași, 24-26 September 2015, Romania. The financial support was from project nr.262/2014, "High performance polymeric insulators for electrical rotating machines. Technology and modeling approaches," the PN II 2013 Partnerships Programme, Romanian Ministry of National Education—Executive Unit for Financing Higher Education, Research, Development and Innovation.

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