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REVIEW

PhD dissertation by Nelson Kiprono Rotich, MSc. entitled:
The role of radiation and conventional techniques in the development of hydrometallurgical processes for the recovery of critical and strategic metals
made under the supervision of prof. dr hab. eng. Andrzej G. Chmielewski from the Institute of Nuclear Chemistry and Technology, Warsaw, Poland

The issue of obtaining critical and strategic metals from ores and post-production waste remains both a significant and current challenge, not only from industrial and ecological perspectives but also from scientific and research standpoints. This topic involves the exploitation of physicochemical phenomena occurring at phase boundaries, utilizing techniques such as leaching, extraction, or flotation. Among the various methods for obtaining critical and strategic metals, including rare earth elements in pure form, hydrometallurgical extraction emerges as a key technique. This approach employs solutions and solvents to process raw materials such as titanium ores, zinc-lead, and copper tailings through leaching. The application of aqueous and/or hydro-organic solutions facilitates the selective isolation of target elements after preliminary purification, enrichment, and final determination. Thus, analytics play a pivotal role in the entire process.

The compatibility of employed methods ensures high recovery rates of pure elements, alongside high quality and repeatability of measurement results. These methods include techniques such as X-Ray Fluorescence (XRF), coupled spectral methods (e.g., ICP-MS), microscopy techniques like SEM, or Neutron Activation Analysis (NAA), utilized in various configurations. Consequently, the broad scope of quality control in products derived from ores, geological materials, and waste after metal processing necessitates improvements in the methodological algorithm. Such advancements aim to enhance the efficiency of metal extraction in pure form and improve isotope recovery by optimizing extractants and process conditions.

The critical phase of technological and analytical procedures involves sample preparation, which employs various physical, physicochemical, chemical, and biological methods to isolate target components from matrices. Therefore, the search for solvents that meet the principles of "*green chemistry*" and improve isolation, purification, and enrichment processes while adhering to the requirements of Good Laboratory Practice (GLP) and Good Manufacturing Practice (GMP) is of particular interest.

The development of novel methodologies and procedures increases the potential for their commercial application, enabling their integration into the monitoring and control of individual stages of technological processes. This makes it possible to use these methodologies in various analytical configurations for industrial and environmental determinations. These issues were the focus of Nelson Kiprono Rotich's, MSc. research.

Upon reviewing this dissertation, I find its interdisciplinary nature particularly noteworthy. It integrates aspects of geology and ecology with the physical chemistry of phase-boundary processes and solution chemistry, extending into radiation chemistry. The research addresses scientifically novel solutions, with its primary aim being the development of methodologies that enable the selective and effective (high recovery and repeatability) isolation of critical and strategic metals from ores and processing waste.

The doctoral dissertation prepared by Nelson Kiprono Rotich, M.Sc. is a comprehensive, monothematic study spanning 214 pages. The dissertation is divided into six parts: introduction, literature review, experimental part (including materials and methods), results with discussion, summary and conclusions, and bibliography (220 references). The work is supplemented by summaries in both Polish and English, a list of acronyms and three appendices, which include: a list of figures - 88 items, tables - 10 items, as well as a list of publications and other achievements of the author.

The literature review introduces the reader to general topics related to the mineralogy and occurrence of critical and strategic elements in ore deposits, providing a characterization and discussion of their chemical and physicochemical properties. Next, the author presented both main and specific (side) objectives, which are clearly outlined, supported by a well-defined scientific hypothesis.

The review of extraction methods for critical and strategic metals progresses from classical Nernstian extraction and leaching to hydrometallurgical techniques, emphasizing acid-base equilibria and the role of radiation in isolating elements and isotopes in pure form. Additionally, the dissertation discusses enrichment techniques and final determination methods using spectral and spectroscopic techniques (e.g., ICP-MS) and imaging methods (e.g., SEM). Overall, this section is well-written and provides an engaging introduction to the topics of mineralogy and elemental analysis.

Nevertheless, the manuscript contains numerous typographical and nomenclature errors, reflecting insufficient linguistic proofreading and preparation. Furthermore, the absence of a summary table outlining the advantages and disadvantages of the described techniques is regrettable. Although some aspects are addressed in referenced works (e.g., *Separation-2023*), such a table would significantly enhance readability.

In my opinion, the dissertation's objectives and hypotheses are clearly and convincingly presented. The methodologies, experimental conditions, measuring equipment, software, statistical analyses, and validation methods are described comprehensively and raise no objections.

The most important achievements of the PhD student include:

1. Application of radiation and conventional instrumental techniques, including X-Ray Fluorescence (XRF), coupled spectral methods with microscopic imaging, and Neutron Activation Analysis (NAA) supported by radiotracers, to identify a wide range of critical and strategic metals (including rare earth elements) obtained through leaching and hydrometallurgical extraction from ores and post-industrial waste.
2. Development of comprehensive, selective methodologies for recovering valuable elements, including critical and strategic metals, from Ti ores and Zn-Pb and Cu tailings (post-industrial waste), this was achieved by optimizing solution mixtures, ingredient concentrations, mixing speeds, temperature, and pH during leaching and extraction processes.
3. Optimization of conditions for the selective complexation and chelation process of strategic and critical metals obtained from ores and post-processing products with the use of specific ligands (page 54), ensuring high recovery and purity of extracted fractions.

4. Demonstration of the reliability of radiotracer methods for real-time monitoring of metal recovery and process dynamics. Research involving D-T neutron generation and NAA significantly contributed to improving process efficiency and metal recovery, especially on laboratory and pilot scales.

5. Comprehensive validation of the analytical procedure across all stages of the research, including statistical analysis, based on methodological descriptors. These validated methodologies appear well-suited for routine industrial applications.

At this point it should be stated that the goal set by the Supervisor and the PhD Student has been achieved. However, I have a few questions and comments about the results obtained:

1. The mechanisms of "binding" isolated strategic and critical metals from real geological samples using complexing ligands are insufficiently explained, e.g. *2,4,5 tris alloxy, 1,2,3 triazine* and/or *tributyl phosphate*. Could you provide more details explaining this process, guaranteeing high recoveries and purity of the obtained fractions?

2. In my opinion, The terms "***optimal***" and "***optimization***" are overused and often applied inconsistently throughout the dissertation. Would "***selection***" or "***choice***" be more appropriate? If optimization is intended, please clarify the methods and criteria employed. Please also explain the differences in nomenclature.

3. I wonder whether the ionic or deep eutectic liquids in the final stages of metal and isotope recovery can improve outcomes? What do you think about this solution? What is your perspective on this approach?

4. Would the use of Field Flow Fractionation for separation, purification and enrichment of extracts meet your expectations as both an analytical and industrial technique, particularly given its compatibility with ICP-MS?

These comments do not diminish the dissertation's substantive value. Some comments can be found as controversial and are intended to provoke discussion and clarification during the public defence.

In accordance with the relevant regulations (Act of July 20, 2018, *Law on Higher Education and Science, in particular articles and regulations;* On academic degrees and scientific titles, together with supplements), the presented dissertation meets the requirements for doctoral theses and I submit to the Council Scientific Institute of Nuclear Chemistry and Technology in Warsaw to admit Mr. Nelson Kiprono Rotich, MSc to further stages of the procedure **to obtain a PhD degree** in chemical sciences, within the field of exact and natural sciences.

Stary Toruń/Toruń, January 8, 2025

prof. dr hab. Bogusław Buszewski