

UNIVERSITY OF JYVÄSKYLÄ
DEPARTMENT OF CHEMISTRY
RESEARCH REPORT NO. 191

VILLE SOIKKELI

**HYDROMETALLURGICAL RECOVERY
AND LEACHING STUDIES FOR SELECTED
VALUABLE METALS FROM FLY ASH
SAMPLES BY ULTRASOUND-ASSISTED
EXTRACTION FOLLOWED BY ICP-OES
DETERMINATION**

Academic Dissertation for
the Degree of Doctor of Philosophy



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ABSTRACT

Soikkeli Ville

Hydrometallurgical recovery and leaching studies for selected valuable metals from fly ash samples by ultrasound-assisted extraction followed by ICP-OES determination

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Au, Co, Cu, Cr, Ir, Ni, Pd, Pt, V and Zn are metals used widely as raw materials in industry. They can all be considered as valuable metals. Out of these metals Co, Cr, Ir, Pd and Pt were recognized as critical raw materials in the ad-hoc working group of the European Commission's report in 2014. While the primary sources of these metals are drying up it seems to be reasonable to investigate new methods to recover the metals from secondary sources e.g., from industrial fly ash.

In this work, new methods for the recovery of all metals (Au, Co, Cu, Cr, Ir, Ni, Pd, Pt, V, Zn) and determination of the noble metals (Au, Ir, Pd, Pt) from fly ash samples were developed. The samples were collected from Finnish power plants using a mixture of biomass and peat as a fuel. An ultrasound-assisted digestion was utilized as a sample pre-treatment method and the concentrations of elements were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). The measurement conditions were optimized by applying a standard reference material, a recovery test and synthetic samples. The determination of the noble metals investigated was found to be affected by spectral interferences due to the emission of matrix elements Cu, Fe, Mn, Si, Ti and W. The interferences were corrected successfully for lines Pd 340.458 and Ir 224.268 nm by the multiple linear regression (MLR) technique.

An ultrasound-assisted leaching procedure with oxalic acid as a leaching agent was developed for the recovery of elements. A leaching rate from 70% to 90% was obtained for the elements investigated. The parameters of extraction were optimized for a sample weight of 10g. Liquid-liquid extraction and sulfide precipitation methods in the recovery of the noble metals from oxalic acid leachate were investigated. The former method was found to be more specific for the noble metals examined and thus preferred to the latter method.

Keywords: Fly ash, precious metal, recovery, ultrasound-assisted extraction, sulfide precipitation, liquid-liquid extraction.

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PREFACE

The work has been carried out by the Department of Chemistry, at the University of Jyväskylä during 2009-2014. First, I would like to express my gratitude to docent Ari Väisänen for the opportunity to work in his research group, and for his encouragement and patient guidance during the work. Ari, the current Head of the Department, Prof. Jan Lundell, the former Head of the Department, Prof. Jussi Valkonen and especially the Development Manager Risto Ryymin from Jyväskylän Energia are gratefully acknowledged for enabling this work and for their collaboration during the research. I would also like to thank the group members Ph.D. Siiri Perämäki and M.Sc. Antti Tiihonen in the Department of Chemistry, Hannu Lamberg and Miikka Tulonen for their collaboration throughout the project. In addition, I thank Aki Ilander, Ph.D. for his co-operation at the beginning of the work.

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Kuopio 19.04.2016

Ville Soikkeli

ABBREVIATIONS

| | |
|-------------|--|
| A | aquatic phase |
| AC | added concentration |
| ALIQ | Aliquat 336®, quaternary ammonium salt |
| A/O | volume ratio (aquatic phase/organic phase) |
| BCR | the European Community Bureau of Reference |
| BTMPPA | bis-2,4,4-trimethylpentylphosphinic acid |
| CC | corrected concentration |
| CRM | certified reference material |
| CSE | conventional sequential extraction procedure |
| DAS | dialkyl sulfide |
| DBC | dibutyl carbitol |
| DBE | dibutyl ether |
| DEM | diethyl malonate |
| EDDS | ethylenediaminedisuccinic acid |
| EDTA | ethylenediaminetetraacetic acid |
| EF | enrichment factor |
| EoL | end-of-life |
| DTPA | diethylene triamine pentaacetic acid |
| FAAS | flame atomic absorption spectrometry |
| FINAS | Finnish Accreditation Service |
| GFAAS | graphite furnace atomic absorption spectrometry |
| GSF | Geological Survey of Finland |
| HIDS | 3-hydroxy-2,2-iminodisuccinic acid |
| ICP-OES | inductively coupled plasma optical emission spectrometry |
| ICP-MS | inductively coupled mass spectrometry |
| LIX® 860N-I | 5-nonylsalicylaldehyde oxime |
| LOD | limit of detection |
| LOQ | limit of quantification |
| L/S | liquid-to-solid ratio |
| MC | measured concentration |
| MIBK | methyl isobutyl ketone |
| MSE | microwave-assisted sequential extraction |
| MLR | multiple linear regression |
| MSW | municipal solid waste |
| NIES | National Institute for Environmental Studies |
| NIST | National Institute of Standards and Technology |
| NTPA | nitrilotriacetic acid |
| O | organic phase |
| PGM | platinum group metal |
| p | statistical probability |
| PTFE | polytetrafluoroethylene |

| | |
|------|---|
| r | correlation coefficient |
| REE | rare earth element |
| Rec. | recovery |
| RSD | relative standard deviation |
| SE | sequential extraction |
| SMT | Standards, Measurement and Testing Programme |
| SRM | standard reference material |
| TBP | tributyl phosphate |
| UASE | ultrasound-assisted sequential extraction procedure |
| UNEP | United Nations Environment Program |

CONTENTS

| | |
|---------------|--|
| ABSTRACT | |
| PREFACE | |
| ABBREVIATIONS | |
| CONTENTS | |

| | | |
|-------|---|----|
| 1 | AIMS OF THE STUDY..... | 11 |
| 2 | INTRODUCTION..... | 12 |
| 3 | REVIEW OF THE LITERATURE..... | 14 |
| 3.1 | Background of the study..... | 14 |
| 3.1.1 | Characterization and utilization of bio fly ashes..... | 14 |
| 3.1.2 | Finnish environmental legislation on waste utilization | 15 |
| 3.1.3 | Commercial recovery of metals from fly ash..... | 15 |
| 3.1.4 | Selection of elements to be recovered from fly ashes | 17 |
| 3.2 | Quality of analytical results | 19 |
| 3.2.1 | Calibration..... | 19 |
| 3.2.2 | Limit of detection and quantification..... | 20 |
| 3.2.3 | Random and systematic errors..... | 20 |
| 3.2.4 | Significance tests | 21 |
| 3.3 | ICP-OES measurements..... | 22 |
| 3.3.1 | Robust conditions of the plasma..... | 23 |
| 3.3.2 | Spectral lines used for analysis of Au, Ir, Pd and Pt..... | 24 |
| 3.3.3 | Spectral interferences on the lines of Au, Ir, Pd and Pt..... | 26 |
| 3.3.4 | Multiple linear regression..... | 27 |
| 3.4 | Ultrasound-assisted sample pre-treatment..... | 28 |
| 3.5 | Sequential extraction methods..... | 30 |
| 3.5.1 | Conventional sequential extraction..... | 30 |
| 3.5.2 | Accelerated sequential extraction procedures for particulate material | 31 |
| 3.6 | The extraction of oxide fraction from fly ash samples | 32 |
| 3.6.1 | Selective leaching of the oxide fraction..... | 32 |
| 3.6.2 | Leaching of oxide fraction by oxalic acid | 32 |
| 3.7 | The recovery of noble metals by liquid-liquid extraction..... | 36 |
| 3.8 | Metal recovery by sulfide precipitation | 37 |
| 3.8.1 | Precipitating agents | 39 |
| 3.8.2 | Effect of temperature and contact time..... | 39 |
| 3.8.3 | Sulfide precipitation of noble metals | 40 |
| 4 | EXPERIMENTAL..... | 41 |
| 4.1 | Samples and reference material..... | 41 |

| | | |
|------|---|----|
| 4.2 | Reagents | 42 |
| 4.3 | Instrumentation..... | 43 |
| 4.4 | Magnetic separation procedure | 44 |
| 4.5 | Ultrasound-assisted digestion procedures | 45 |
| 4.6 | Digestion in an autoclave | 45 |
| 4.7 | Sequential extraction procedures | 46 |
| | 4.7.1 Conventional sequential extraction procedure..... | 46 |
| | 4.7.2 Ultrasound-assisted sequential extraction procedure..... | 48 |
| 4.8 | Ultrasound-assisted extraction by oxalate reagents | 48 |
| 4.9 | Sulfide precipitation procedure ¹⁸⁹ | 49 |
| 4.10 | Solvent extraction procedure | 49 |
| 5 | RESULTS AND DISCUSSION..... | 51 |
| 5.1 | Calibration | 52 |
| 5.2 | Magnetic separation of Co, Cr, Cu, Ni, V and Zn from fly ash | 52 |
| 5.3 | Ultrasound-assisted digestion procedures | 53 |
| 5.4 | Total element concentrations in real fly ash samples | 54 |
| 5.5 | The determination of Au, Ir, Pd and Pt by ICP-OES | 56 |
| | 5.5.1 Initial interferences observed | 57 |
| | 5.5.2 Multiple linear regression (MLR) model | 61 |
| | 5.5.3 Recovery test for precipitate samples | 66 |
| 5.6 | Ultrasound-assisted sequential extraction of fly ash samples | 66 |
| | 5.6.1 Total leachable concentrations of Co, Cr, Cu, Ni, V and Zn... 66 | |
| | 5.6.2 Optimization of sonication time in step iii..... | 70 |
| | 5.6.3 The element concentrations in oxide fraction..... | 70 |
| | 5.6.4 Ultrasound-assisted extraction methods using ammoniumoxalate and oxalic acid | 71 |
| 5.7 | Sulfide precipitation | 80 |
| | 5.7.1 Initial precipitation experiments..... | 80 |
| | 5.7.2 Effect of precipitation agent..... | 81 |
| | 5.7.3 Effects of pH..... | 81 |
| | 5.7.4 Added concentration of sulfide | 82 |
| | 5.7.5 Effect of temperature | 83 |
| | 5.7.6 Effect of contact time | 83 |
| | 5.7.7 Optimized sulfide precipitation procedure | 84 |
| 5.8 | The recovery of valuable metals by solvent extraction..... | 85 |
| | 5.8.1 Effect of pH and temperature..... | 87 |
| | 5.8.2 Effect of A/O ratio | 88 |
| | 5.8.3 Effect of extraction time | 89 |
| 6 | CONCLUSIONS..... | 90 |
| | REFERENCES..... | 92 |

1 AIMS OF THE STUDY

- a) To determine the total concentrations of the valuable metals (Au, Ir, Pd, Pt, Co, Cu, Cr, Ni, V and Zn) from different bio fly ash samples,
- b) evaluate and correct the spectral interferences in the determination of the noble metals (Au, Ir, Pd and Pt) concentrations from the fly ash samples by ICP-OES,
- c) study the leaching behavior of the valuable elements by sequential extraction procedure,
- d) develop a fast and accurate extraction procedure by which the valuable metals could be recovered from the fly ash with as pure fraction as possible
- e) study the feasibility of solvent extraction and sulfide precipitation methods in the recovery of the noble metals from the fly ash leachate.

2 INTRODUCTION

Since the rapid industrialization, especially in developing countries, the demand for metals is increasing. In 2014, the ad-hoc working group of the European Commission determined the elements which will be critical resources in the near future: Be, Co, Cr, Ga, Ge, In, Mg, Nb, Si, Sb, W, the platinum group metals (PGMs; Pd, Pt, Rh, Ru, Os, Ir) and rare earth elements (REEs: Y, Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu).¹ The Au, Cu, Ni, V and Zn, elements mined commercially from Finnish soil were not considered to be regarded as critical resources due to their relatively low supply risk. In addition to low supply risk the economic importance of Au was considered to be low. However, the economic importance of Ni, V and Zn was evaluated as being extremely high (EU 2014). Of the critical resources Co, Cr and PGMs are mined commercially in Finland.² In Europe, the natural sources of PGMs are highest in the region of Fennoscandia.³ In the mineralized area of Finnish Lapland adsorption of Au into the twigs of the juniper plant⁴ and crowberry⁵ has been reported.

The primary sources of metals possessing high market value are depleting which gives rise to the investigation of new methods to recover metals from secondary sources e.g. fly ash.⁶ The recovery of these metals from municipal solid waste (MSW) ash^{7-9,10}, sewage sludge fly ash¹¹⁻¹³, coal¹⁴⁻¹⁵ and coal gasification fly ash¹⁶ is discussed in some works. Jung and Osako⁷ evaluated that concentrations of Ag, Cu, In, Pd and Zn in MSW fly ash was almost equal to that in the Japanese ore used for the recovery of these metals. Hydrometallurgical metal recovery methods usually consume less energy than pyrometallurgical methods and can be more selective in the recovery of specific metal. The recovery of metals from coal fly ashes is a widely studied area and numerous hydrometallurgical

recovery methods of Ga, Ge, Ni, V and Zn from coal fly ash have been proposed.¹⁴ Hydrometallurgical recovery methods for Cu^{17,18} and Zn^{19,20} from MSW fly ash, Ni and V from heavy fuel oil fly ash^{21,22} while for Ga²³, Ge²³ and V¹⁶ from coal gasification fly ash have been introduced in papers. However, the hydrometallurgical recovery of metals from bio fly ashes is a less studied area. Recently, Perämäki introduced methods for the determination and recovery of REEs from biomass and peat fly ash samples.²⁴ Many trace elements, including hydrolyzed cations e.g. (Cu²⁺, Co²⁺, Ni²⁺, Zn²⁺) have been reported to be captured inside the oxide fraction of soil samples by sorption mechanism²⁵. In the works of Pöykiö *et al.*^{26,27} notable portions of Co, Cu, Ni, V and Zn were separated by extraction which attacked the oxide fraction of the bio fly ash. In such extraction a dilute organic acid solution can be used as an extracting agent. This can be considered a more environmental friendly extraction than the extraction method of using mineral acids or synthetic chelating agents. The consumption of the extracting agent can also be lower since only the part of the fly ash is extracted.

In some works, an organic acid, oxalic acid, has been preferred to HNO₃ and HCl as an extracting agent in the extraction of Al²⁸, Cr²⁹, Fe²⁸, Mn²⁹, Ti²⁸ from MSW fly ash. The separation of PGMs and Au from basic metals by solvent extraction is largely carried out by exploiting the differences in the chemistry of their anionic chloro-complexes.³⁰

Some metals are separated commercially by precipitating them as sulfides. For example in the Talvivaara company's production process Co, Cu, Ni and Zn were precipitated as sulfides from a pregnant solution and sold as such to refineries.³¹ Compared to hydroxide and carbonate precipitation metals can be removed from a solution more specifically at a low pH, as the precipitate settles better. Additionally, after smelting the precipitates they can re-used further.³²

3 LITERATURE REVIEW

3.1 Background of the study

3.1.1 Characterization and utilization of bio fly ashes

It has been estimated that globally 780 million tons of coal fly ash while 480 million tons of bio fly ash is generated per year.³³ In Finland, approximately 500 x 10³ tons of fly ash per year from the combustion of peat and biomaterial is generated as a by-product of power and electricity production.³⁴ There is a wide acceptancy that the combustion of the latter fuel does not contribute to the greenhouse effect.³⁵ Currently biomass covers 8-15 % of the world`s energy supplies but the portion has been estimated to rise and, by 2050, to be 33-50 %.³⁵

Primary components in bio fly ash are oxides e.g.



The chemical and physical properties, as well as the mineral composition, of fly ash from the combustion of wood³⁷ and straw³⁸ as well as from the co-combustion of wood with oil^{38, 39}, coal³⁹ and peat³⁹ have been thoroughly reviewed by other authors.^{37, 39} A pure wood ash usually contains higher concentrations of Ca, K, Mg and Cl than ash from the co-combustion of wood with peat and/or coal.³⁷ Co-combustion of coal or peat with wood adds concentrations of Al, Fe, Mg and S to the fly ash.³⁹ Thus, coal fly ash is usually more abundant in Fe₂O₃ and thus contains more magnetic material than bio fly ash.³³ Factors such as the location of the fuel collected, the composition of the fuel, the type of combustion technique and the combustion temperature influence the elemental composition of the resulting ash.³⁷

The composition of biomass differs from coal as it is more variable—especially with respect to moisture, structural components and inorganic

constituents – than the composition of coal.⁴⁰ Bio fly ash can be regarded as more water-soluble than coal fly ash. Up to 61 % of straw fly ash³⁸ while only 0.2-7.2 % (mean 1.6 %) of coal fly ash⁴¹ has been found to be water-soluble. This gives rise to the study of metal recovery from bio fly ash by extraction.

On combustion most of the organic material of the fuel is volatilized. However, the unburnt carbon remains in the ash. Thus the metals are more concentrated in the ash than in the original fuel. The elements having a tendency to enrich in the fly ash are mainly those that become volatile and then partly condense in the flue gases of the combustion system. These include As, B, Bi, Cd, Ge, Hg, Mo, Pb, S, Se, Sb, Sn and Ti.⁴² Air classification tests have shown that trace elements (Co, Cr, Cu, Mn, Pb, V, Zn) were enriched on particles of the smallest size (< 38 µm) of fly ash.⁴³

Global utilization of coal fly ash^{44, 45}, waste⁴⁶ and biomass fly ash⁴⁶ have been reviewed in the literature. An estimate is that half of the bio fly ash generated annually in Finland, approximately 250 000 tons, can be utilized for different purposes e.g. as a fertilizer in soil³⁷, a hardener in filling mine cavities⁴⁷, an ingredient in cement manufacturing⁴⁸, and road pavement and soil amendment while half is landfilled. In Finland, the prerequisite for the utilization of the fly ash is the fulfilling of the requirements set by the legislation.^{49, 50}

3.1.2 Finnish environmental legislation on waste utilization

The prerequisite for utilization of bio fly ash is the fulfilling of the requirements set by the legislation.^{49, 50} In order to harmonize the legislation for waste with the European Union, the new Waste Act⁵¹ came into effect at the beginning of May 2012 in Finland. The definition of waste was determined in the law and a five-stepped waste hierarchy (prevention of waste formation, preparation for reuse, recycling, other reuse, and final treatment) EU directive came into effect with the law.⁵² In the new Waste Tax Act⁵³ which came into effect at the beginning of 2011, fly ash is regarded as waste and all landfills in Finland were included in the waste legislation rules. From the beginning of 2015 the landfilling of fly ash cost 55 € per ton. Additionally, transporting the ash always increases costs. If material is regarded as a byproduct or it fulfills the requirements of the End-of-Waste Criteria of the EU Directive⁵⁴ it must be registered under the REACH process. Utilization of energy production ashes require REACH registration if they are handled other than mechanically or reused elsewhere other than where they are formed. For fertilizer use the decree 403/2009⁴⁹ sets minimum concentrations for nutrients and maximum values for heavy metals. In the decree the limit values for soil construction⁵⁰ are given both for total and leachable concentrations of elements.

3.1.3 Commercial recovery of metals from fly ash

In a study by Morf *et al.*⁸ the fractionation of 31 elements including Au, Ag, Pt, Rh and REEs in ash samples from the MSW combustion process was evaluated. The conclusion was that the application of the Thermo-Re® concept on solid

waste incineration bottom ash enriched the concentrations of these metals while producing energy during the incinerating process.

The first pilot plant to recover heavy metals from fly ash, by using an acidic flue gas cleaning solution, while also thermally destroying organic compounds from filter ash by the 3R-process was reported in 1990 by Vehlow.⁵⁵ However, the process was thought not to be economically feasible. The research carried out at the University of Munich resulted in a process by which Zn can be separated from MSW fly ash with the final purity of 99.99 % by the FLUREC process.²⁰

Stages in the suggested procedure are:

- i) leaching of fly ash by HCl,
- ii) liquid-liquid extraction in two counter-current mixer-settler units at constant pH by 30 % (m/m) BTMPPA (bis-2,4,4-trimethylpentylphosphinic acid, dissolved in a refined petroleum product (number of carbons predominantly between 9 and 16)
- iii) stripping by 2.5 mol l⁻¹ H₂SO₄ and
- iv) electrolysis.

The concentration of Zn in the solution after stage iii is 48-fold to the concentration in the original filter ash. The process is said to be economically sustainable as the remaining fly ash can be returned to its recovered substance cycle and there are savings in waste water treatment costs²⁰. However, according to the economic analysis of Fellner *et al.*, with the FLUREC process only 25% of extractable Zn can be recovered at production costs in the range or slightly above the current market price for Zn.⁵⁶ This is contributed to i) by low concentrations of Zn (1500-15000 mg kg⁻¹) in the fly ash, ii) the leaching of Zn occurring significantly at pH < 4 which requires high volumes of HCl, and iii) because the extraction rate of Zn is 75 % at best. Additionally, they concluded that of the total European Zn import, only 2.2 % could be, in theory, substituted by recovering it from MSW fly ash formed inside the EU.⁵⁶

At Chalmers University of Technology, in Gothenburg, Sweden, recovery methods for Cu^{17, 18} from MSW fly ash have been developed. A suggested recovery method consists of four steps:

- i) leaching of ash by 3 mol l⁻¹ NH₄NO₃ for 24 hours by L/S 5,
- ii) liquid-liquid extraction by LIX® 860N-I (5-nonylsalicylaloxime) (diluted by kerosene), A/O 1:1, one stage,
- iii) stripping by 2 mol l⁻¹ H₂SO₄, A/O 1:1, one stage and
- iv) electrolysis.

Yields of 95% for Cu were obtained in laboratory tests. The calculations revealed that at 100% the yield of Cu and its base assumes that a recycling rate of the reagent kerosene of over 99% is required in order to process and be economically beneficial. In another study, by using the recycled acidic process of water as an extracting agent all Cu and Zn were leached from bark ash.⁵⁷ A physical separation method based on magnetic density separation of the ash particles to recover precious elements from MSW bottom ash has been developed

at the Delft University of Technology, in the Netherlands.⁵⁸ Nowadays, a company named Inashco utilizes the technology on a commercial scale.⁵⁹

3.1.4 Selection of elements to be recovered from fly ashes

Many chemists agree that the following elements form the group of noble metals: all elements from the platinum group metals (Ru, Rh, Pd, Os, Ir, Pt), Au, and Ag. Some chemists also include Hg in the group. The commonality for all noble metals is that, unlike most base metals, they are resistant to corrosion and oxidation in any conditions. Ir, Pd and Pt are technologically important metals which industry has found use for, for example, in medicine, computers, cars and catalysts^{30,60}. The majority of Au is used in jewelry, electronics and for investment purposes.⁶¹ These metals possess economical value due to their low natural abundance and complicated extraction and refining processes.⁶¹ In some works Au^{8, 15, 58}, Ir¹², Pd¹²⁻¹³ and Pt^{8, 12, 13} have been found with notable concentrations from different incinerator ashes. Thus, these elements were included in the study and are referred as "noble metals" later on the text.

Cu and Zn were chosen since the recovery of them from fly ash has been studied earlier by other groups (3.1.3). The studies have shown that the metals Co, Cu, Cr, Ni, V and Zn are present as a group in minerals in Finnish soils.⁶² A Geological Survey of Finland (GSF) has mapped the main metallogenic zones of Finland (Figure 1). In April 2014, Au, Co, Cr, Cu, Ni, Pd, Pt and Zn were mined from Finnish soil.⁶³ In December 2012 Mustavaaran Kaivos Oy submitted an Environmental Permit application to the authorities regarding the mine and concentrating plant in order to commercially mine and refine vanadium.⁶⁴ A thorough book covering the use of Co, Cr, Cu, Ni, V and Zn in different industrial purposes is available.⁶⁵

At the moment the end-of-life (EoL) recycling rates of the selected metals, according to a United Nations Environment Program (UNEP) Report are: V < 1%, Au 15-20%, Zn 19-60%, Ir 20-30%, Cu 43-53%, Ni 57-63% Pd 60-70%, Pt 60-70%, Co 68% and Cr 87-93%.⁶⁶ A term "valuable metal" is used throughout in the text to cover the investigated elements in this work: Au, Ir, Co, Cr, Cu, Ni, Pd, Pt, V and Zn.

SUOMEN METALLOGEENISET VYÖHYKKEET

The main metallogenic zones of Finland

70°E

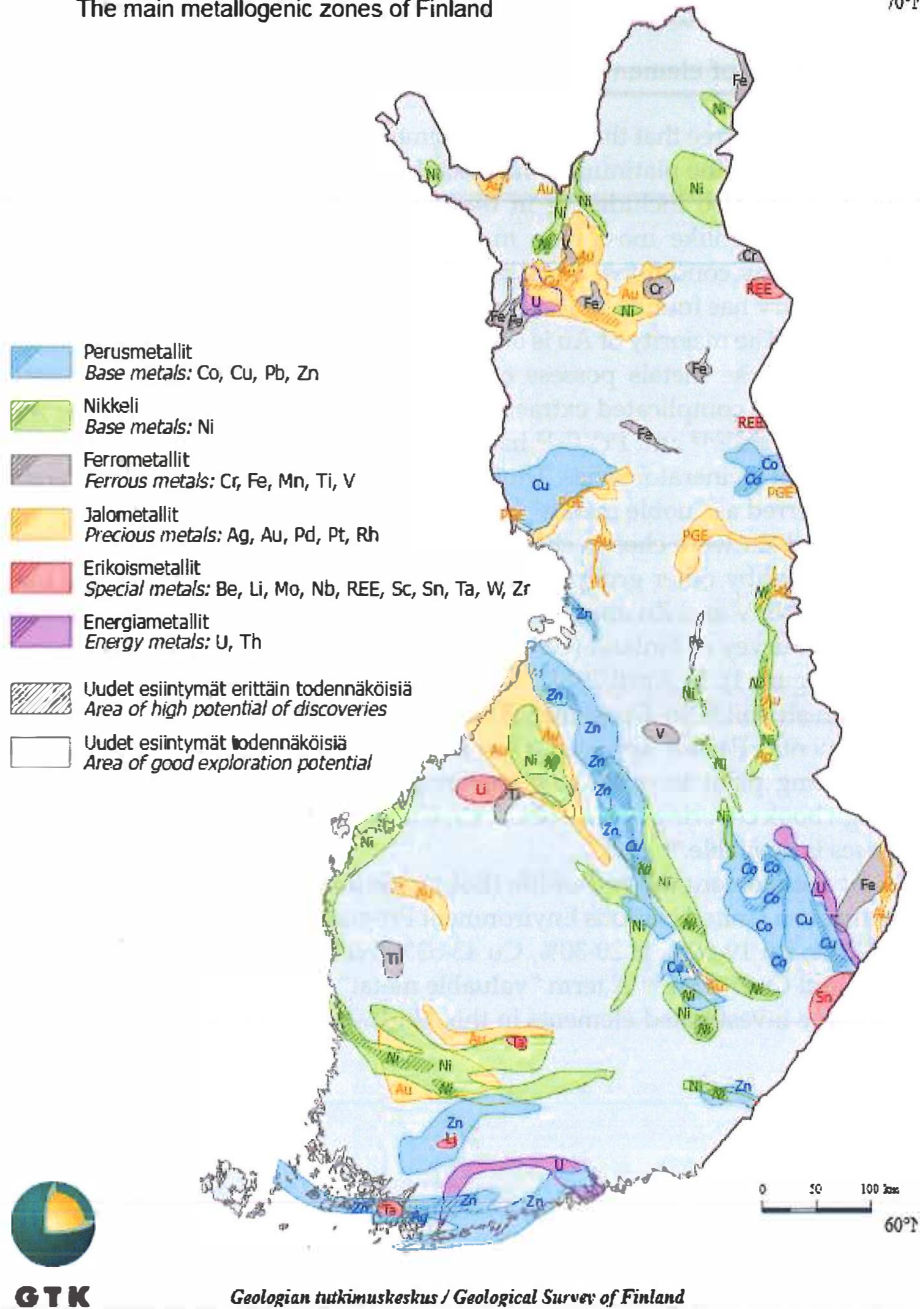


FIGURE 1 The main metallogenic zones of Finland.⁶⁷

3.2 Quality of analytical results

The aim of this work was to develop an analytical method by which selected valuable elements could be recovered from fly ash samples. The determination of them from the fly ash matrix posed a challenge since the concentrations of them were notably lower than the concentrations of the matrix elements. Additionally, the emission of the matrix elements produce always matrix effects (3.3.1) in ICP-OES technique. In the validation of the analytical method the following parameters were included: linearity, accuracy, precision, limits of detection and quantification and robustness.

Robustness of both ICP-OES instruments (4.3) was confirmed. The linearity was evaluated by calibrating the instrument before each measurement. By applying a SRM sample systematic errors in the analysis were evaluated. A deviation of determined analyte concentration from certified analyte concentration of SRM gave information of the accuracy of the method. The relative standard deviation of measured concentrations of four replicate samples gave information of the precision of the method. The determination of LOD and LOQ was essential in this work since the concentrations of some analytes were low. Significance tests were applied to evaluate the feasibility of the multilinear regression (MLR) correction method.

3.2.1 Calibration

The basis of determination by instrumental techniques is a linear dependency of response on the concentration of analyte in the sample. In the ICP-OES technique, after complete excitation of atoms and ions the atoms and ions return from excited state to ground state. The energy difference between the energy states and thus the wavelength at which the emission occurs is specific for each element. The more excited atoms and ions of elements in the sample, the higher emission intensity for the element is obtained. However, the conditions of measurement (sample introduction, state of the plasma, sample matrix) may vary. Thus, in analytical determination the calibration must be carried out before every measurement series.

The calibration is usually performed by measuring a blank solution and at least three standard solutions when the matrix matching technique is used. The matrix element concentrations of the blank and standards are adjusted to be similar to real samples. The blank solution is prepared in the same way as the standards with the exception that it does not contain the analyte or analytes. The emission of the blank solution is subtracted from the emission of the standards. From calibration data the equation of the calibration line in the form of:

$$y = bx+a, \tag{1}$$

is calculated. In the equation y is an emission of analyte, b is the slope of the line and a is its intercept on the y -axis. The emission is plotted in the y -axis as a

function of the concentration. The source of error in calibration for emission of standards is usually in the range of 1-3% and is thought to originate from measurements, while the error in preparing the standards can be evaluated as < 0.3 %. Random errors of the intercept (s_a) and slope (s_b) of the calibration line must always be calculated from the calibration data.

The first prerequisite of calibration is that the magnitude of emission must be linear in the calibration range. Usually this is the case in the ICP-OES technique. However, when high concentrations are measured self-adsorption may occur and result in non-linear response.⁶⁸ Secondly, the analyte concentrations of the standard solutions cover the range where the concentration of analyte is in the measured samples.⁶⁹ The quality of the calibration curve can be evaluated by the linear regression method. The method is based on the calculation of the correlation coefficient, r , which describes how well the experimental points fit into the calibration line. It is calculated by the equation:

$$r = \frac{\sum_{i=1}^n \{(x_i - \bar{x})(y_i - \bar{y})\}}{\{\sum_{i=1}^n (x_i - \bar{x})^2 (y_i - \bar{y})^2\}^{1/2}}, \quad (2)$$

where the points $(x_1, y_1), (x_2, y_2), \dots, (x_n, y_n)$ are the total number of calibration points, and \bar{x} and \bar{y} are mean values calculated for the individual calibration points⁶⁹. The correlation coefficient, r , can take values $-1 \leq r \leq 1$. A perfect positive correlation gives $r = 1$ while perfect negative correlation $r = -1$.⁶⁹ Usually r values over 0.999 are accepted for calibration in analytical measurement in the ICP-OES technique.

3.2.2 Limit of detection and quantification

Especially when low concentrations of analytes are measured it is essential to know whether or not the signal of analyte can be distinguished from the signal of the blank or background signal. By definition, the limit of detection (LOD) of an analyte is the concentration of the analyte which gives an instrumental signal significantly different from the blank of the background signal.⁶⁹ The limit of quantification (LOQ) is defined as the lower limit for precise quantitative measurements. The most common way to calculate the LOD and LOQ from calibration data in ICP-OES measurements is to substitute $(y_b + 3s_b)$ and $(y_b + 10s_b)$ into the calibration line $y = bx + a$, respectively.⁶⁹ In terms y_b is the signal of blank solution and s_b is the random error of the slope of the calibration line.

3.2.3 Random and systematic errors

In analytical chemistry, random and systematic errors cause the determined value to deviate from the true value.⁷⁰ The total error observed is the sum of random and systematic errors. It must be emphasized that random errors are always present. It is important to avoid systematic errors throughout the analysis. The systematic error in sampling is not discussed here as it is not in the scope of this thesis. A thorough guide of technical requirements of sampling for

accreditation from the Finnish Accreditation Service (FINAS)⁷¹ is available. The systematic error in sample pre-treatment can originate for example from the loss of analyte in the extraction process and in adsorption of it into walls of glassware, contamination of reagents or glassware or an untrue measured value of scale or micro pipette if the calibration of them has been neglected. In a measurement by ICP-OES systematic error can originate from problems in sample introduction, changes in conditions of plasma or gas flows, and from spectral interferences. The precision of the analytical measurement is typically evaluated by analyzing from three to six replicate samples.⁷² When the same analysis procedure is carried out for all replicate samples the results can be thought to be subject to random errors.⁷⁰ Thus, results of replicate determinations are considered to be a random sample from a normal population of results. The standard deviation, s , of this distribution is usually called the precision of the procedure.⁷⁰

Standard reference materials (SRM) and certified reference materials (CRM) can be used to evaluate the accuracy of the analytical measurement. This can be done by comparing the determined concentrations of the analytes to the certified concentrations of the analytes in the reference material. The common method is to analyze a CRM or SRM with a matrix composition as similar as possible to the real samples. The use of CRM is recommended since the material has a certificate for element concentrations. In the certification process the concentration of desired analytes are determined in selected laboratories by different analytical techniques. Finally, the certified element concentrations are reported in the certificate with a certain level of uncertainty related to a specific concentration level.⁷³

3.2.4 Significance tests

In order to decide whether the difference between the means of two populations (e.g. experimental and certified value) can be attributed to systematic error a statistical test known as a significance test can be employed⁶⁹. Significance tests are widely used in evaluating whether or not the difference of the mean or standard deviation of the mean obtained by two methods is significant. This kind of test, the two-sided t-test, is applied if there is no assumption that one of the methods produces higher means than the other one. In significance tests the truthness of a *null hypothesis*, H_0 , is tested. If null hypothesis is true the difference of the means obtained by two methods is solely due to random error. Assuming that the null hypothesis is true, a statistical test evaluating the probability of truthness of null hypothesis is followed. A common way is to reject the null hypothesis if its probability is less than 5% implying that in less than 1 of 20 cases the null hypothesis could be true. If the calculated test value exceeds the critical test value with the respective degrees of freedom found in statistical tables⁶⁹ the null hypothesis is rejected. However, it is of great importance to compare standard the deviations of the results obtained by the two methods before applying a test for comparison of the means. It can be tested with the F-test by

which the two sample variances, namely the squares of the standard deviations, are compared:

$$F_{(v_1, v_2)} = (s_1^2 / s_2^2), \quad (3)$$

where 1 and 2 are chosen so that F is always ≥ 1 . The number of degrees of freedom of the numerator and denominator are $n_1 - 1$ and $n_2 - 1$, respectively. If the calculated F -test value exceeds the critical test value with the respective degrees of freedom found in statistical tables the difference of precision between the methods is significant.

The paired t -test can be used for the statistical comparison of leached element concentrations by two different sample pre-treatment methods when the concentration levels of different elements in samples are at different levels.⁷⁰ The means for concentration of each element for both methods is calculated from the replicate samples. Then, a pairwise comparison for the means of each element between the analysis methods is performed. The t -value of the test can be calculated as follows:

$$t = \frac{\bar{x}_d}{s_d} \sqrt{n}, \quad (4)$$

where n is the number while \bar{x}_d and s_d are the mean and standard deviation of the differences of all the pairs, respectively.⁶⁹

A prerequisite for the test is that differences between the pairs should contain both positive and negative values implying that residuals of the differences are normally distributed⁶⁹. If the calculated t -test value exceeds the critical test value with the degrees of freedom of $(n - 1)$ the difference of means between the methods is significant at the confidence limit of 95% and null hypothesis should be rejected.

3.3 ICP-OES measurements

In inductively coupled plasma optical emission spectrometry (ICP-OES) all free metal atoms and ions are excited from the ground state to the excited state at as high temperature as 10 000 K. When the atoms and ions return back to ground state they emit energy which can be registered using optics either in the ultraviolet area (100-380) or in the visible area (380-800 nm). The amount of energy is dependent on the amount of atoms or ions and thus on the concentration of elements in the sample. The dependence of emission intensity on the concentration of analyte is valid in a broad concentration area, which enables the determination of elements in a concentration of from $\mu\text{g l}^{-1}$ to g l^{-1} .⁷⁴ This reduces the need for diluting the samples and thus saves time. Each element should be measured using an atom or ion emission line which should be distinctive with respect to emission lines of other elements in the sample.

As with other spectrometric techniques (inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS)), the technique is subject to interferences. The matrix of samples, especially easily ionized elements (EIEs)⁷⁵, and especially Na⁷⁶ and acids⁷⁷⁻⁷⁸ may affect the atomization, ionization and excitation processes. These effects can be substantially reduced by using the robust conditions of the plasma (3.3.2), and by using internal standards and the matrix matching technique. Due to high operating temperature and comparatively long residence time for the sample in the plasma the chemical interferences are few.⁷⁵ More severe interferences, the spectral interferences, encountered in using the technique are discussed in 3.3.3.

3.3.1 Robust conditions of the plasma

The use of robust conditions in ICP-OES leads to an efficient energy transfer between the plasma and the sample.⁷⁹ Plasma can be made robust by optimizing the atomization, ionization and excitation processes.⁸⁰ The robustness of the plasma is referred to as its ability to keep the variation of an analyte signal to a minimum when the matrix composition changes.⁷⁷ The thermal capability i.e. the closeness of plasma to a local thermodynamic equilibrium is classically studied by observing the ionic-to-atomic ratio, most classically that of Mg II (280.270 nm)/Mg I (285.213 nm)⁸¹ but comparisons of lines Cr II (267.716)/Cr I (357.868) and Ni II (231.604 nm)/Ni I (232.138 nm) have also been reported.^{79, 82} The Mg lines are favored since the wavelengths are relatively close, the intensities of the ionic and atomic lines are of the same magnitude and transition properties are known to have an acceptable accuracy.^{77, 82} When the line intensity ratio is > 8 the plasma is said to work under robust conditions.⁷⁷

The matrix effects in the axial view have been found to be more severe than in the radial view.⁸³ However, by using robust conditions the matrix effects in the axial view caused by Na⁸⁴ and CH₃COOH⁷⁸ have been minimized to the same extent as for radial viewing. Robust conditions have been associated with the high power of the generator, low carrier gas flow rate and large diameter of the injector.⁸⁵ The robust conditions have been obtained by using RF power > 1.3 kW and the nebulizer gas flow rate 0.5-0.8 L min⁻¹.^{76, 80, 86-90} The emission signals of Au^{91, 92}, Ir⁹¹, Pd^{91, 92} and Pt^{91, 92} have been seen to decrease linearly as a function of Na concentration in the sample. The phenomenon was enhanced by increasing the concentration of HCl.⁹¹ In⁹³, Sc⁹² and Y^{92, 93} have been used as internal standards in order to minimize the interferences in the aforementioned processes in the determination of Au, Pd and Pt. Mokgalaka *et al.*⁹² It was found that changes in the emission signals of the PGMs due to power variations could be effectively compensated using either Sc or Y as internal standards. For variations in the aerosol gas flow rate, both Sc and Y enabled compensation for Pd and Au between flow rates of 0.60 and 0.80 l min⁻¹ and for Pt at 0.80 l min⁻¹. By using Sc as an internal standard Pt was determined successfully at Na concentrations < 5000 mg l⁻¹.

3.3.2 Spectral lines used for analysis of Au, Ir, Pd and Pt

ICP-MS has been the dominant technique in the determination of Au^{8, 15, 94}, Ir¹², Pd^{12, 13} and Pt^{8, 12, 13} from ash samples. The technique enables lower limits of detection than ICP-OES. However, ICP-OES has been widely used in the analysis of Au, Ir, Pd and Pt from different samples e.g. ore, rock, jewellery alloys and spent catalysts (Table 1).^{91-93, 95-108}

Three analytical lines for the determination of Au, two for Ir while four analytical lines for the determination of Pd and Pt from different samples by ICP-OES have been used. It must be emphasized that in reported works there are huge differences between the composition of the samples analyzed. The determination of noble metals from a single metal standard solution can be regarded as an easier analytical task than the determination of them from a sample containing matrix elements e.g. ore or fly ash. In the first case, lines with lower sensitivity, for example Pd 360.955 nm and Ir 212.680 nm can be used while the more sensitive lines Au 242.795 nm/267.595 nm, Ir 224.268 nm, Pd 340.458 nm, Pt 214.423 nm/265.945 nm are required in the latter case. All in all, the lines Au 242.795 nm, Pd 340.458 nm, Pt 265.945 nm and Ir 212.680 nm are most favored in the reported works (Table 1).

TABLE 1 Suggested analytical lines (nm) in the determination of Au, Pd, Pt and Ir from different samples by ICP-OES.

| Matrix | Au | Pd | Pt | Ir | Ref. |
|---|------------------------|-----------------|-----------------|-----------------|-------|
| Gold alloy | 208.21/242.795/267.595 | | | | [93] |
| Converter matte | 242.795/267.595 | 340.458 | 214.423/265.945 | | [92] |
| Jewelry alloy | 267.595 | 340.458 | 265.945 | | [95] |
| High purity gold | | 340.458 | 214.423 | | [96] |
| Copper concentrate | 242.795 | | | | [97] |
| Single metal standard solution | 267.595 | 360.955 | 265.945 | 212.680 | [91] |
| Copper-nickel sulfide ore | 242.795 | 340.458 | 265.945 | 212.681 | [100] |
| Copper ore | 242.795 | 340.438* | 214.423 | | [99] |
| Rocks, ores, concentrates, sulfide floats | 242.795 | 340.458 | 265.945 | | [102] |
| Monolith catalyst | | 340.458/324.270 | 265.945/299.797 | | [98] |
| Auto-catalyst | | 229.651 | 203.646 | | [102] |
| Automobile catalyzer | | 340.458 | 265.945 | | [104] |
| Platinum ore | | 229.65 | 265.945 | | [98] |
| Vehicle exhaust particulates | 242.795 | 340.458 | 214.423 | 224.268 | [105] |
| Road dust | | 340.458 | 214.423 | 212.680/224.268 | [103] |
| Rock | | 360.955 | 214.423 | 212.681 | [108] |

*reported in paper, where probably a 340.458 nm line was used.

3.3.3 Spectral interferences on the lines of Au, Ir, Pd and Pt

A major source of interference in the ICP-OES technique is spectral interference originating from the emission of matrix elements and Ar in the vicinity of the emission line of analyte.⁷⁴ Emission spectra in ICP-OES is line-rich: 5250 lines for Ce, 4400 emission lines for Fe, 3800 for W and 3400 Mo lines are known. The spectral interferences caused by the matrix elements Al, Ca, Fe, K, Mg, Na, P and Ti on different analytes have been investigated in the papers of Daskalova *et al.*¹⁰⁹ while Petrova *et al.*⁹⁸ reported 74 lines (Fe 38, Mn 19, Ti 11, Al 4, Ca 1, Mg 1) interfering with the determination of Pd, Pt and Rh. Bio fly ashes which contain all these elements and thus the spectral interferences are encountered in the analysis. Due to the high market value of the metals, the accurate determination of Au, Ir, Pd and Pt is of primary importance. One plausible option to overcome the problem could be the use of the multiple linear regression (MLR) technique. The technique has been used in the evaluation of spectral interferences in the determination of As^{80, 110, 111}, Au^{106, 106}, B¹¹²⁻¹¹³, Ca¹¹⁴, Cu⁸⁰, Fe¹¹⁵, Mg¹¹⁶, Pb^{80, 110}, S¹¹⁷, Sb^{80, 111}, Si¹¹³, Sn¹¹¹ and Zn⁸⁰.

Spectral interference can be divided into four categories: simple background shift, sloping background shift, direct overlap, and complex background shift.¹¹⁸ These interferences can be corrected by background correction¹¹⁹, inter-element correction¹²⁰ and multiple linear regression techniques.¹¹⁰ Modern ICP-OES instruments enable the observation of spectra after the measurement and utilization of the spectrum library.¹²¹ In this chapter, the discussion is restricted to the spectral interferences of Au, Ir, Pd and Pt and the multiple linear regression method.

The spectral interference of matrix elements on Au, Ir, Pd and Pt lines have been studied typically by determining the analyte concentrations from synthetic samples containing both the analyte and the matrix elements with known concentrations.^{98, 99, 106} In the solutions the matrix element concentrations have been 10-1000 times higher than the analyte concentration. From the synthetic sample with the following concentrations: Fe 1000 mg l⁻¹, Au, Pd and Pt 1 mg l⁻¹ concentrations of 1.2, 1.2 and 1.4 mg l⁻¹ were determined by using the analytical lines Au 242.795, Pd 340.458 and Pt 214.423 nm, respectively⁹⁹. In another work the line Pt 214.423 nm was found to be interfered with by the line of Cd when [Cd]:[Pt] was > 1.25:1 in the samples. Additionally, the line Au 242.795 nm was found to be interfered with when the Fe concentration was over 20-fold the Au concentration.¹⁰⁰ Unfortunately, many authors have reported spectral interference on noble elements but neither the wavelength of interfering line(s) nor the concentration of the interferent(s) have been reported.

The interfering emission lines of the matrix elements in the vicinity of the emission lines of Au, Ir, Pd and Pt in the ICP-OES technique are presented in Table 2. It can be seen that for line Au 242.795 nm twelve, while for the line Au 267.595 nm six interfering lines have been reported. Some lines e.g. Pt 265.945 nm and Pd 340.458 nm are not recommended because of complete spectral overlap with other emission lines.¹⁰³ On the basis reported in the literature, the major

interferents for Au, Ir, Pd and Pt reported have been Cu, Fe, Mn, Ni and Ti. The interference from some of the Fe emission lines on the lines of Au, Ir, Pd and Pt has been reported, with one exception (Pd 229.651 nm, Table 2). Fe, Mn and Ti have interfered with at least one line of Au, Pd and Pt. The line Ir 224.268 nm has been interfered with by Cu, Fe and Ni. The lines Au 267.595, Ir 224.268 and Pt 214.423 nm have not been affected by the emission of Mn nor Ti while the line Pd 340.458 nm has not been affected by the emission of Mn. Spectral interference of Si on the emission lines of Au, Ir, Pd and Pt has not been reported in any paper available.

TABLE 2 Interfering emission lines of the matrix elements in the vicinity of emission lines of Au, Ir, Pd and Pt in the ICP-OES technique.

| Analyte line (nm) | Interfering line (nm) | Ref. |
|-------------------|---|---------------------|
| Au 242.795 | V 242.73 (i), W 242.75 (i), W 242.781 (i), Cr 242.792 (+), Mn 242.798 (+), Ta 242.800 (+), Pt 242.804 (+), Ti 242.823 (+), Fe 242.829 (+), V 242.83 (i) | [99][100][106][122] |
| Au 267.595 | Cr 267.568 (+), U 267.588 (+), Co 267.598 (+) Fe 267.611 (+) | [107] |
| Ir 224.268 | Fe 224.18 (i), Ni 224.29 (i), Cu 224.262 (+) | [100][122] |
| Pd 229.651 | Mn 229.645 (i), Ti 229.654 (i) | [122] |
| Pd 324.270 | Ti 324.199(i), Fe 324.227 (i), Fe 324.311 (i), Mn 324.378 (i), | [98] |
| Pd 340.458 | Ce 340.413 (i), Fe 340.436 (i), V 340.44 (i), Ti 340.50 (i), W 340.53 (i), Zr 340.483 (i) | [103][122] |
| Pt 203.646 | Ti 203.602 (i), Mn 203.605 (i), Fe 203.643 (i), Ti 203.681 (i) | [101] |
| Pt 214.423 | Fe 214.44 (i), Al 214.54 (i), Fe 214.52 (i) | [122] |
| Pt 299.797 | Fe 299.785 (i), Mn 299.789 (i), Fe 299.806 (i) | [98] |

i = interference on the analytical line reported

+ = increase of emission signal on the analytical line reported

3.3.4 Multiple linear regression

In the papers mentioned in the previous chapter only in the works by Roy and Mistry⁹⁹ and Torgov *et al.*¹⁰⁰ have the proportional interferent to analyte concentration levels causing the interference on the analytical lines been reported. If the emission signal of the analyte is known to be linearly dependent on the concentration of the interferents, the analyte concentrations can be corrected using the multiple linear regression (MLR) technique.

In one study¹⁰⁶ the interference effects of the matrix elements (Cr, Fe, Mn, Pt, Ta, Ti and W) on the determination of Au at 242.795 nm were successfully eliminated by the MLR technique (Table 2) when the Au concentration was over 0.7 mg l⁻¹. Unfortunately, the MLR expression lines were not reported in the paper. MLR is an extended version of simple linear regression⁶¹ in which one response variable, *y*, depends on the number of predictor variables and can be presented mathematically in the form of

$$y = \beta_0 + \beta_1 x_{1i} + \beta_2 x_{2i} + \dots + \beta_p x_{pi} + e_i, \quad (5)$$

where y_i (the dependent variable) is the measured concentration of analyte from sample matrix solution i , β is the regression coefficient, the x_{pi} terms are the independent variables i.e. the measured concentrations of matrix elements in the sample solution, and e_i are independent random variables with normal distribution.¹²³ The technique is based on the analysis of synthetic samples containing both the analytes and the interfering elements at five levels of concentrations.^{110, 111, 113, 124} The prerequisite for carrying out multiple regression is that the number of calibration solutions must be greater than the number of predictor variables. Additionally, the correlation between the regression lines must be lower than 0.2.^{72, 80, 113, 124} As a result a multiple linear regression line is formed. It contains all the terms (intercept and element(s)) which explain significantly ($P < 0.05$) the measured analyte concentration. The corrected concentration for each analyte is obtained as the measured concentrations of elements are multiplied by respective coefficients of the multiple expression line. For example, in the work of Väisänen and Ilander⁸⁰ the spectral interferences on the Cu 327.393 nm line, in axial measurement, was eliminated by substituting measured Mn, Si and Cu concentrations (mg l^{-1}) into the following MLR expression line:

$$\text{Cu 327.393: } y = -0.607 + [0.00625\text{Mn}] + [0.0242\text{Si}] + [0.990\text{Cu}].$$

3.4 Ultrasound-assisted sample pre-treatment

Ultrasound is a sound wave with a frequency ranging from 20 kHz to 10 MHz¹²⁵ and thus is not audible by humans. A major difference from electromagnetic waves is that ultrasound waves require a media in order to proceed. When ultrasound waves travel in liquid media expansion and compression cycles occur. The expansion phase pulls molecules apart while the compression phase pushes the molecules together.¹²⁶ If the ultrasound power is high enough it can form bubbles in liquid media. The cycle in which the bubbles form, grow and implode is called cavitation.^{125, 127, 128} Rapid adiabatic compression of gases and vapors within the bubbles or cavities produces extremely high temperatures and pressure in localized "hot spots" (estimated at about 5000 °C and 2000 atm., respectively).¹²⁹ Ultrasound releases a lot of energy and provides mechanical and chemical effects thus speeding up the extraction. Ultrasound improves the analyte solubility and diffusivity of the solvent inside the solid particles, the solvent penetrability and transport.¹²⁶ Additionally, more analyte comes into contact with the solvent while hydroxyl and hydrogen peroxide radicals are effective in oxidizing the organic material.¹²⁶

Ultrasound-assisted extractions can be carried out using a water bath, probe or novel ultrasonic processor called a cup-horn sonoreactor.¹³⁰ It has been reported that an ultrasound water bath lacks uniformity in the distribution of

ultrasound energy inside the water bath.¹²⁶ However, in a study by Ilander and Väisänen⁸⁷ it was proven statistically by an ultrasound field homogeneity test that significant differences in element concentrations were not observed between the samples digested at different locations in the ultrasound water bath. Also a decline of power with time has been stated as a drawback in the bath technique.¹²⁶

The advantage of sonication in a water bath is high sample treatment capacity which usually is an essential need in laboratories handling a series of samples during a working day. An ultrasonic probe has the advantage over a water bath that it focuses its energy more locally and thus provides more efficient cavitation in the liquid. However, the use of strong acids is not enabled in the technique. A cup-horn sonoreactor combines the advantages of bath and probe (Table 3).¹³⁰ It is possible to extract six samples at the same time. The ultrasound water bath enables a rapid sample treatment of 30 samples.⁸⁸ In addition to the centrifuge tube ultrasound-assisted digestion can be performed successfully, for example, in an Erlenmeyer flask using higher sample weight.

TABLE 3 The main characteristics of an ultrasonic bath, ultrasonic probe and cup-horn sonoreactor.¹³⁰

| Feature | Bath | Probe | Cup-horn sonoreactor |
|----------------------------|-----------|------------|----------------------|
| Intensity ($W\ cm^{-2}$) | 1-5 | 100 | 50 |
| Distributed energy | Irregular | Regular | Regular |
| Amplitude | Fixed | Adjustable | Adjustable |
| Type of sonication | Indirect | Direct | Indirect |
| Sample throughput | High | Low | Medium |
| Sample volume (ml) | Variable | 1-50 | 1 |
| Contamination risk | No | Yes | No |
| Erosion tip | No | Yes | No |
| Cost | Low | High | High |

From the sidepoint of green chemistry, by using ultrasound the extraction processes can be shortened and only a low volume of reagents is required. Additionally, performing the extraction at an ambient temperature results in safer working practices. Compared to microwave digestion, which requires operating temperatures of at least 150 °C¹³¹ or more, less control of temperature and pressure is needed.¹³² Ultrasound-assisted sample pre-treatment has been successfully used in elemental analysis of particulate material e.g. bottom ash, fly ash, sediment, soil and sewage sludge.^{110, 133-137}

Ultrasound-assisted methods in the recovery of valuable metals from fly ash samples

The use of ultrasound-assisted sample pre-treatment with the aim of recovering valuable metals from fly ash samples is not reported widely. 100% of Ag was leached from certified reference material BCR176-R (city waste incinerator fly ash) by two-step extraction using a cup-horn sonoreactor¹³⁸. In the steps the reagents and sonication times were as follows:

- i) 25% (v/v) HNO₃, 25% (v/v) HF, 5% (v/v) HCl, 20 min of sonication.
- ii) 0.3% (m/v) CH₄N₂S, 2% (v/v) H₂SO₄, 10 min of sonication.

Hasegawa *et al.* investigated the recovery of “rare-termed” metal contents: B, Ce, Co, Dy, Eu, Ga, Gd, Hf, In, Li, Lu, Mn, Nb, Nd, Ni, Pr, Rb, Sb, Se, Sm, Sr, Ta, Tb, Te, Ti, Tm, V, W, Y, and Yb from three industrial fly ash samples.¹³⁹ In their methodology the fly ashes were extracted in an ultrasound water bath at an ambient temperature for 6 h using extremely dilute solutions (0.01 mol l⁻¹) of ethylenediaminetetraacetic acid (EDTA), [S,S] ethylenediaminedisuccinic acid (EDDS), and 3-hydroxy-2,2-iminodisuccinic acid (HIDS) as extracting agents. The sonication notably increased the recovery of Li, W and slightly the recovery of B, Sr and V.¹³⁹ They assigned this with the destruction of the crystalline structure of the ash which happened due to the mechanochemical effect induced by the ultrasound irradiation. Namely, the metals inside the crystal structure may not be extracted without breaking the crystalline lattice structure of the solid particles.

3.5 Sequential extraction methods

3.5.1 Conventional sequential extraction

The results of total digestion give information on total or pseudo-total concentrations of elements. However, neither the speciation of the elements nor their bound mechanism to material can be deduced. Instead, from the results of the sequential extraction method, this can be evaluated better. In the methodology of sequential extraction, the sample is extracted sequentially in numerous stages using a series of reagents to sub-divide the total metal content.¹⁴⁰ The “strength” of the treatment increases at each stage. Thus, the leachability of elements in different natural conditions can be evaluated. The most used sequential extraction schemes are from Tessier *et al.*¹⁴¹ and the revised BCR scheme¹⁴² developed originally by the European Standards, Measurement and Testing Programme (SMT, formerly the European Community Bureau of Reference). The schemes have been validated for sediment samples. The former scheme¹⁴¹ distinguishes leachable fractions into:

- i) exchangeable,
- ii) bound to carbonates,
- iii) bound to Fe-Mn oxides,
- iv) bound to organic matter and sulfides,
- v) residual fraction.

The steps in the latter protocol¹⁴² are labelled according to the chemical processes occurring in the extraction and not after the target mineral phases, as in the Tessier¹⁴¹ protocol.

Some authors have applied a BCR or modified BCR sequential extraction scheme to evaluate the suitability of Finnish wood²⁶, wood and peat^{27, 143, 144} and coal fly ash¹⁴⁵ to forest fertilizer use. In these works the results have been compared to the limit values set in the Decree on Fertilizer Products 24/11 by the Finnish Ministry of Agriculture and Forestry.⁴⁹ In the scheme of Nurmesniemi *et al.*¹⁴³ an additional step preceding the steps of i-iii of the revised BCR sequential extraction scheme was included. During the additional step the fly ash was washed with water (pH adjusted to 4.0) in order to evaluate the leaching of elements from landfill-dumped fly ash when rainwater passes through it. Recently, such a washing step (with distilled water) belonged to a sequential extraction method which otherwise followed the protocol of Tessier *et al.*¹⁴¹ A Tessier-based extraction method was used to evaluate the leachability of the elements having considerable market value, Ti, Zr, Hf, from industrial coal fly ash.¹⁴⁶

3.5.2 Accelerated sequential extraction procedures for particulate material

A drawback with conventional sequential extraction procedures is their long sample extraction time, namely, 17.5 hours in the Tessier¹⁴¹ scheme and 50.5 hours in the revised BCR¹⁴² sequential extraction scheme. Ultrasound-assisted sequential extraction (UASE) procedures performed in a water bath for different sample matrixes e.g. contaminated soil¹⁴⁷, lake sediment^{148-150, 149, 151} and sewage sludge¹⁵² have been reported.

In addition to UASE microwave-assisted sequential extraction (MSE) procedures have been utilized in the extraction of particulate material. The UASE procedure for SRM 1648 (Urban Air Particulate Matter)¹⁵³ resulted in similar recoveries for Cu, Mn and Zn while lower recoveries of Fe than by conventional sequential extraction were obtained.¹⁵³ MSE procedures for SRM1633b (Coal Fly Ash)¹⁵⁴ and NIES CRM No. 8 (Vehicle Exhaust Particles)¹⁵⁵ were carried out. In these protocols the total extraction time was from two to slightly over three hours.

3.6 The extraction of oxide fraction from fly ash samples

3.6.1 Selective leaching of the oxide fraction

It is known that the oxide fraction is a “sink” of metals.¹⁵⁶ Manganese oxides are known to have a high sorption capacity for many trace elements, including oxyanions (e.g., molybdate, phosphate, selenite, arsenate) and hydrolyzed cations (e.g. Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+}).²⁵ These elements can be strongly adsorbed by oxide surfaces. The association of trace elements with Fe^{157} and Mn^{25} oxide material in lateritic soil has been evaluated in a few papers. In these papers, selective dissolution techniques for oxide material are developed. The conclusion was that Cr was associated mainly with Fe oxides, Cu, Ni, and V were associated with both Fe and Mn oxides, and Co was associated mainly with Mn oxides.²⁵

In the original scheme from Tessier *et al.*¹⁴¹ the hydrous oxides of Fe and Mn are extracted together by $0.04 \text{ mol l}^{-1} \text{ NH}_2\text{OH}\cdot\text{HCl}$ in 25% CH_3COOH at 96°C . Extraction using $0.1 \text{ mol l}^{-1} \text{ NH}_2\text{OH}\cdot\text{HCl}$ at an ambient temperature, recommended in the original BCR scheme¹⁵⁸, releases metals mainly from amorphous manganese oxide phases with little attack on the iron oxide phases¹⁵⁶. In the revised BCR sequential extraction¹⁴² scheme the same fraction is extracted using $0.5 \text{ mol l}^{-1} \text{ NH}_2\text{OH}\cdot\text{HCl}$ at pH 1.5 at an ambient temperature. This provides an effective attack on the Fe oxide phases while still releasing metals from Mn oxide phases.¹⁵⁶ Davidson *et al.*¹⁵⁹ carried out sequential extraction according to a) the revised BCR protocol and b) the revised BCR protocol except that in stage ii $0.2 \text{ mol l}^{-1} (\text{NH}_4)_2\text{C}_2\text{O}_4$ (pH 3) instead of $0.5 \text{ mol l}^{-1} \text{ NH}_2\text{OH}\cdot\text{HCl}$ (pH 1.5) was used. They reported that higher recoveries of Fe and Cu were obtained in step ii by using the latter method. For the recovery of Ca and Pb the method was not recommended since the elements readily precipitate as oxalates.

3.6.2 Leaching of oxide fraction by oxalic acid

Oxalic acid vs. mineral acids and synthetic chelating agents

The most widespread leaching method for fly ash samples is to use mineral acids (HNO_3 , HCl and H_2SO_4) since many metals form soluble cations and the non-silicate matrix of the ash is dissolved. However, especially in the case of highly alkaline fly ash, their consumption may be high. Additionally, numerous liquid-liquid extraction steps are required to separate the precious metals from the solution. After the liquid-liquid extraction the neutralization of the waste mineral acid solution requires high volumes of alkali.

In some works fly ash samples have been leached using the synthetic chelating agents ethylene diamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA) and nitrile triacetic acid (NTPA) with promising recoveries for Cr¹⁶⁰, Cu¹⁶⁰⁻¹⁶¹, Li¹³⁹, Ni¹⁶², V¹⁶², W¹³⁹ and Zn.¹⁶⁰ The drawback in using synthetic chelating agents is that they are not biodegradable and their leakage into the environment might cause secondary pollution.¹⁶³

Organic acids are biodegradable and can be used as natural chelating agents which form metal complexes with the target metals. Thus, from the environmental point of view, the organic acids in the leaching of fly ash samples can be preferred to mineral acids and synthetic chelating agents.¹⁶³

Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, is an organic acid, which is used commercially in textile manufacture and processing, metal surface treatment, leather tanning, cobalt production and in the separation and recovery of REEs.¹⁶⁴ As with other dicarboxylic acids, it reacts with various metals to form metal salts.¹⁶³ The use of it in the extraction of Al, Fe, Mn, Co, Cr, Cu, V and Zn from fly ashes has been reported in numerous papers (Table 4). In the papers the fly ashes have been extracted typically by using solutions of 0.1-1 mol l⁻¹ $\text{H}_2\text{C}_2\text{O}_4$ and equimolar mineral acids (HNO_3 , HCl , H_2SO_4) have also been used in the extraction for comparison. $\text{H}_2\text{C}_2\text{O}_4$ has been preferred to all mineral acids in the extraction of Al and Fe, to HNO_3 and HCl in the extraction of Cr and Mn and to H_2SO_4 in the extraction of Ge.^{28, 29, 163, 165-166} On the other hand Co, Cu, Mn and Zn have been recovered at notably higher concentrations using mineral acids than by $\text{H}_2\text{C}_2\text{O}_4$.^{28, 161, 163} Although 1 mol l⁻¹ H_2SO_4 was preferred to the aforementioned acids in the extraction of Cr and Mn, the use of 1 mol l⁻¹ HCl was recommended in extraction.²⁹ However, equal recoveries of Al, Fe, Cu and Zn were obtained when $\text{H}_2\text{C}_2\text{O}_4$ and mineral acids were applied in the extraction tests.¹⁶¹

Oxalic acid compared to other organic acids

Organic acids have been used as reagents in the extraction of bottom and fly ash samples.^{163, 165, 167} By using $\text{H}_2\text{C}_2\text{O}_4$ higher leached concentrations of Al¹⁶⁵, Fe¹⁶⁷, Mn¹⁶⁵ and Zn¹⁶⁷ were obtained than by extracting the samples by malic acid ($\text{C}_4\text{H}_6\text{O}_5$), tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$), citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and gluconic acid ($\text{C}_6\text{H}_{12}\text{O}_7$). However, in some works $\text{C}_6\text{H}_8\text{O}_7$ has been preferred to $\text{H}_2\text{C}_2\text{O}_4$ in the extraction of Al^{163, 167}, Fe¹⁶³, Cu¹⁶³, Pb¹⁶³ and Zn¹⁶³. The high Fe leaching yield of $\text{H}_2\text{C}_2\text{O}_4$ was speculated to be attributed to the formation of soluble FeC_2O_4 .¹⁶⁵ Low recoveries of Ca and Pb were attributed to low solubility of CaC_2O_4 and PbC_2O_4 .¹⁶³

The effects of temperature, L/S ratio, extraction time and sonication

The effect of temperature in the extraction of Cu, Mn, Fe and Ti from tire waste fly ash samples by 1 mol l⁻¹ oxalic acid has been reported in one study.²⁸ When the temperature was raised from 23 °C to 60 °C 5 times more Cu, 4 times more Mn while 2 times more Fe and Ti were extracted. Zhang and Itoh²⁹ extracted MSW fly ash samples by oxalic acid at ambient temperature and at 150 °C but, unfortunately, reported only the results obtained at 150 °C.

As can be seen from Table 4 the L/S ratios and extraction times reported in other works for the oxalic acid extraction on fly ash samples differ widely. This can be attributed to different matrixes in the samples and different extraction procedures used in the works.

In the work of Anjum *et al.*¹⁶⁷ sonication of the fly ash samples in a water

bath resulted in nearly two-fold recoveries of Al, Fe and Zn compared to extraction without sonication.

TABLE 4 Recoveries of Al, Fe, Mn, Co, Cr, Cu, V and Zn from fly ash samples by oxalic acid extraction reported in the literature.

| Type of fly ash | [H ₂ C ₂ O ₄ , mol L ⁻¹] | L/S (ml g ⁻¹) | T [°C] | t [h] | Al | Fe | Mn | Co | Cr | Cu | V | Zn | Ref. |
|---------------------------|---|---------------------------|--------|--------|------|------|------|-----|------|------|-----|------|-------|
| Coal | 0.06 | | 25 | 2 | | | | | 10.9 | | 9.1 | | [167] |
| MSW | 0.1 | 100 | 30 | | 100 | ~50 | ~70 | | | 100 | | ~85 | [164] |
| MSW | 0.1 | 40 | 25 | 1 | 43.3 | 46.5 | | | | 45.8 | | 44.9 | [162] |
| Sawdust | 0.1 | | | 24 | | | | | 62 | 81 | | | [168] |
| Hospital MSW (US) | 0.1 | | 28 | 5/10 d | 52.0 | 87.3 | | | | | | 88.0 | [166] |
| Hospital MSW (Without US) | 0.1 | | 28 | 5/10 d | 30.2 | 46.4 | | | | | | 45.3 | [166] |
| MSW | 0.5 | 5 | 25 | 24 | <4 | <1 | <1 | | | 1 | | <1 | [160] |
| MSW | 0.5 | 100 | 30 | | ~82 | ~52 | ~60 | | | 100 | | ~65 | [164] |
| MSW | 1 | 5 | 150 | 5 | 7.8 | 6.9 | 36.6 | 5.9 | 16.6 | 0.5 | 8.5 | 9.2 | [29] |
| tire waste | 1 | 20 | 23 | 24 | 85 | 41 | 5.5 | ND | | 1 | | 0.6 | [28] |
| tire waste | 1 | 20 | 60 | 24 | 108 | 86 | 27 | 3.7 | | 5 | | 0.5 | [28] |

3.7 The recovery of noble metals by liquid-liquid extraction

The term liquid-liquid extraction, a synonym for solvent extraction, refers to a distribution of solute (organic or inorganic) between two immiscible liquid phases in contact with each other.^{168, 169} The analyte is extracted by a suitable reagent to a water-insoluble organic phase.^{168, 170} Finally, the analyte is stripped from the organic phase back into the aquatic phase. Usually, the removal of impurities e.g. by dilute HCl is required in order to obtain a pure fraction of analyte.⁶¹ After each step of extraction, the phase with lower density remains on the top of the solution and the phases can be separated. The efficacy of liquid-liquid extraction can be evaluated by calculating the distribution ratio or separation factor. The first implies how the analyte is distributed between the phases while the latter describes the ability to separate two analytes from each other. Usually the aim of liquid-liquid extraction is to enrich the metal concentrations and finally obtain as pure a fraction as possible. The technique is widely used both in scientific research of chemistry and in industry.

The use of liquid-liquid extraction in the commercial refinement of U was already reported in the late 1940s.¹⁷¹ At least three principal platinum group metal refineries have used the technology since 1995.⁶¹ The separation of PGMs and Au from basic metals by liquid-liquid extraction is largely carried out by exploiting the differences in the chemistry of their anionic chloro-complexes.³⁰ The oxidation state of metal, the pH and the matrix of the sample all contribute to complex formation with the metal and ligand. The low oxidation state favors the ligand change reaction in which chloride ions bound to metals are substituted for organic ligands which contain long aliphatic carbon chains.⁶¹ This decreases the polarity of the metal complex which favors the transfer of the complex into the organic phase. The PGMs form more stable complexes than basic metals⁶¹ in the chloride medium. The heavier the donor atom in the ligand the more stable a complex is formed. Approximately, the order of stability is: S ~ C > I > Br > Cl > N > O >> F.⁶¹ However, to back extract the metal from the organic phase to the aquatic phase the metal complex needs to be broken. The extractant is usually diluted by an organic solvent, or aliphatic or cyclic hydrocarbon, to improve the solubility of analytes and to prevent the formation of third phase.¹⁷² In industrial applications kerosene is usually used as solvent. Solvent extraction reagents can be divided into three categories¹⁶⁸, based on their extracting mechanism:

- i) acid and chelating acid extractants
- ii) anion exchangers
- iii) solvating extractants.

Acid and acidic extractants extract metals by chelating or cation exchange mechanism.¹⁷⁰ Compound with long hydrocarbon chain and the hydroxyoxime group has been reported in the extraction of Pd (II) and Au (III) from chloride solution.^{61, 173}

Anion exchangers are usually based on high molecular weight amine extractants.¹⁶⁸ Tertiary and quaternary amines protonate more readily than a weak base e.g. tri-n-butylphosphate.³⁰ Thus, the amines can be used as ion-exchangers at low acid concentrations while weaker anion-exchangers require higher acid concentration.³⁰ The use of tertiary amines Alamine® 300 (tri-n-octyl amine) and Alamine® 336 (tri-octyl/dodecyl amine) and quaternary ammonium salt Aliquat 336®, the registered trademarks of BASF SE, have resulted in high recoveries of Ir¹⁷⁴, Pd¹⁷⁵ and Pt.¹⁷⁵⁻¹⁸¹

Ethers, esters, ketones, aldehydes and alcohols in tandem with organophosphoric acid derivatives with O or S as an electron donor atom form the group of solvating extractants. Dibutyl carbitol (DBC) and methyl isobutyl ketone (MIBK), dialkylsulfide (DAS) and tri-n-butylphosphate (TBP), extractants in group iii, are used commercially in the extraction of Au, Pd and Pt from chloride media, respectively.^{61, 182} However, low hydrophobicity (DBC), low stability against acid and a slow extraction rate (DAS) and low recovery (TBP) has been reported.¹⁸² A mixture of CH₄N₂S and HCl has been suggested to strip the solution in order to back extract Pt^{176-178, 181-183} from the tertiary/quaternary amine phase to the aquatic phase. Additionally, the same solution has been suggested in the back extraction of Au from the monoamide phase¹⁸³, Pd from the TBP phase¹⁷⁹, and Pd from the oxime phase to the aquatic phase.¹⁷⁶

3.8 Metal recovery by sulfide precipitation

Sulfide precipitation is widely used for removing metals from industrial wastewaters and in effluent treatment.¹⁸⁴ Sulfide precipitation has advantages over the hydroxide and carbonate precipitation methods. Metals can be removed more specifically and quickly, settle better, and it is possible to smelt the precipitates.³² The majority of the literature on the sulfide precipitation of metals discusses the removal of Cr, Cu, Mn, Pb and Zn from soil, sludge, fly ash leachates^{185, 186} and waste water.^{184, 187} Additionally, the method has been used for metal recovery purposes. For example in the production process of the Talvivaara company Co, Cu, Ni and Zn were recovered as their respective sulfides after precipitation.¹⁸⁸ The recovery of PGMs by sulfide precipitation^{189, 191} and electrochemical sulfide precipitation¹⁹⁰ has been patented but hardly discussed in scientific papers.

The thermodynamic equilibria involved in sulfide precipitation can be expressed as³²:





The speciation of sulfide is highly dependent on the pH and at pH < 4 all sulfide is present as H₂S.³² The formation of hydrogen sulfide gas occurs when precipitation is carried out in acidic conditions. To avoid this, the pH of the solution was adjusted to 5 before the addition of sulfide in the work of Feng *et al.*¹⁹² In two other works the precipitation has been followed after the adjustment of the pH by NaOH.^{185, 186} The hydrolysis of C₂H₅NS to H₂S is dependent of pH and, additionally, of the temperature of the solution since more collisions between molecules occur as the temperature rises¹⁸⁴. Thus, by adjusting the pH and temperature the hydrolysis of C₂H₅NS and thus the concentration of sulfide ions liberated into the solution can be controlled.¹⁸⁴ The optimized addition speed of 0.15 g S²⁻/min per 1 l of processed solution at the laboratory temperature has been reported.¹⁹³ The solubilities of metal sulfides e.g. AgS, CuS, CdS, NiS, PbS, ZnS and NiS are lower than the respective hydroxides (Figure 2). This feature has enabled the specific removal of Cu, Ni and Zn from waste water in the sequence of Cu (pH 1.5-2) < Zn (pH 4.5) < Ni (pH 6.5-7.5).^{184, 187} Jandova *et al.*¹⁹³ maintained that the separation of Cu (pH ≈ 1), Co (pH ≈ 3) and Ni (pH ≈ 3) as sulfides from concentrated manganese solution was successful. From a totally different sample, cyanide solution, Au, Pd, Pt, Co and Cu were recovered as sulfides with recoveries over 95% at pH 0.5.¹⁹¹ Additionally, 20-28% of Pd and 20-39% of Au were precipitated in pH 5.5-9.5 when the pH of the solution was adjusted using NaOH. The matrix of samples and the precipitating reagents used were different in different works which probably explains the differences of the optimized pHs reported.

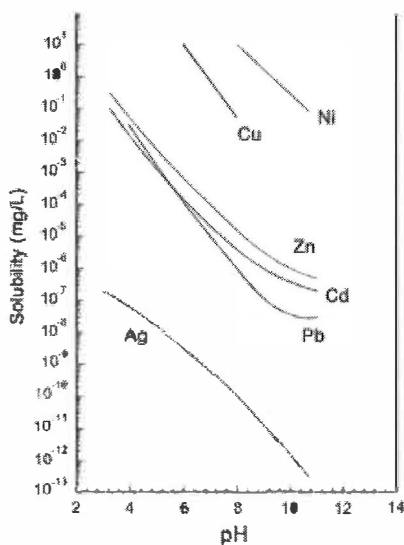


FIGURE 2 Solubility of some metal sulfides as a function of pH.¹⁹⁴

In the study where Ni and Co were precipitated in a batch reactor as sulfides, hydroxides and carbonates it was observed that at the time interval of 0-100 min the settling rate of sulfide precipitate was slowest.¹⁹⁵ After 100 min the settling rate of sulfide precipitate was fastest. This was attributed to the formation of extremely fine sulfide particles which is thought to occur due to the mechanism of homogenous nucleation, aggregation and attrition occurring in precipitation.¹⁹⁶ If the particles are smaller in diameter than 45 μm they are not retained in filter paper.¹⁹⁶ The drawback related to sulfide precipitation is the difficulty in controlling the sulfide dose in precipitation. From the environmental point of view, a hydrogen sulfide gas must be removed using a scrubber. The control of the dissolving rate of H_2S gas^{196, 197} and using $\text{C}_2\text{H}_5\text{NS}$ ¹⁸⁴ instead of Na_2S and NaHS as the source of sulfide, are recommended in papers.

3.8.1 Precipitating agents

In the precipitation of metal sulfides from solution, either aqueous or gaseous sources of sulfide can be used.¹⁹⁸ In reported works, sulfide has been added as Na_2S (aq)^{162, 185, 187}, Na_2S (g)¹⁹⁶, NaHS (aq)¹⁹⁹, $(\text{NH}_4)_2\text{S}$ (aq)¹⁹³ and $\text{C}_2\text{H}_5\text{NS}$ (aq).¹⁸⁴ Karbanee *et al.* reported that the precipitation of NiS occurred only by using a gaseous source of sulfide.¹⁹⁸ Due to the addition of NaOH at pH 4-5 in the first step of two-staged precipitation the volume of expensive precipitating reagent Na_2S was reduced almost 200 times compared to when it was solely applied at pH 7-8.¹⁸⁶ The addition of sulfide by a 1.15-1.2 fold concentration compared to precipitated metals in solution has been reported.^{184, 191} Interestingly, as reported in the papers of Gharabaghi *et al.*¹⁸⁴ and Lewis *et al.*¹⁹⁶, when sulfide was added in excess it was observed that sulfide was present in the remaining solution with less concentration than expected from the stoichiometry. The authors speculated the reason to be the oxidation of sulfide and formation of polysulfide metal complexes in solution. Excess concentration of sulfide can also have the effect of the redissolving of formed precipitate and thus consume the excess sulfide.^{184, 196}

3.8.2 Effect of temperature and contact time

The increase in temperature from 25 $^{\circ}\text{C}$ to 90 $^{\circ}\text{C}$ was reported to increase the precipitation of Pt and Au but not that of Pd, Co, Cu and Ni. The reagent applied was NaHS .¹⁹¹ In another work, the precipitation of Cd, Cu, Ni and Zn was found to increase linearly as a function of the temperature at 45-85 $^{\circ}\text{C}$ ¹⁸⁴ and of the reaction time at 5-45 min. This was attributed to more H_2S molecules formed in the hydrolysis reaction of $\text{C}_2\text{H}_5\text{NS}$ at higher temperature as more collisions between molecules occurred.

3.8.3 Sulfide precipitation of noble metals

It must be noted that no standard method for sulfide precipitation of noble metals is available. A recovery method by which Au and PGMs are precipitated as sulfides is patented.¹⁹¹ In the patent platinum-group metals (Pd, Pt, Rh, Ru, Ir, Os) and Au are precipitated as sulfides in tandem with basic metals from cyanide solution at pH 2. The suggested reagents in precipitation of Au and PGMs were Na_2S and NaHS .¹⁹¹ The authors have concluded that after the precipitation both the basic metals and the noble metals can be recovered and precious metal concentrate can be delivered to precious metals refineries.

4 EXPERIMENTAL

4.1 Samples and reference material

Two different bio fly ash samples which originated from the combustion of wood residues and two ash samples from the co-combustion of wood residue and peat were investigated (Table 5). Additionally, fly ash samples from the co-combustion of peat/coal and sludge/peat (the accurate composition of the fuel is not known) were utilized. Certified reference material SRM1633b (Coal Fly Ash)²⁰⁰ certified by the National Institute of Standards & Technology was used.

TABLE 5 Samples and reference material used in this work.

| Bio fly ash samples | Wood/peat ash samples | Peat/coal/sludge fly ash samples |
|---------------------|-----------------------|----------------------------------|
| Bark ash | Wood 80%/peat 20% | Peat/coal ash |
| Wood roots | Wood 35%/peat 65% | Sludge/peat ash |
| | | SRM1633b (Coal Fly Ash) |

4.2 Reagents

All reagents and standard stock solutions were of analytical reagent grade. PerkinElmer supplied the single standard stock solutions (1000 mg l^{-1}) of Au, Ir, Pd and Pt which were used in the preparation of calibration solutions for the quantitative measurement. Multi-element calibration standard solutions, 10 mg l^{-1} with respect to each element (Table 6), also supplied by PerkinElmer, were used in the preparation of calibration solutions for the quantitative measurement. The reagents used are presented in alphabetical order in Table 7. Ultrapure water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$ (ELGA, Buckinghamshire, UK) was used throughout.

TABLE 6 Element content of multi-element calibration standard solutions, supplied by PerkinElmer.

| Standard solution | Elements |
|--|---|
| Single-element standard (1000 mg l^{-1}) | Au, Ir, Pd, Pt |
| Multi-element standard 3 (10 mg l^{-1}) | Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V, Zn |
| Multi-element standard 4 (10 mg l^{-1}) | Au, Hf, Ir, Pd, Pt, Rh, Ru, Sb, Sn, Te |
| Multi-element standard 5 (10 mg l^{-1}) | B, Ge, Mo, Nb, P, Re, S, Si, Ta, Ti, W, Zr |

TABLE 7 The chemicals used in this work.

| Chemical | Supplier | Purity/Concentration |
|---------------------------------|-----------------|---|
| Acetic acid | Fluka | ≥ 99.0 % |
| Aliquat 336® (quaternary amine) | Sigma-Aldrich | 98.0 % |
| Ammonium hydroxide solution | Sigma-Aldrich | puriss p.a., approx.. 25 % NH ₃ |
| Ammonium acetate | Sigma-Aldrich | ≥ 98.0 % |
| Ammonium chloride | Riedel-de-Haën | ≥ 99.5 % |
| Ammonium oxalate monohydrate | Sigma-Aldrich | ≥ 99.0 % |
| Diethylmalonate | Sigma-Aldrich | ≥ 98.0 % |
| Dibutyl ether | Sigma-Aldrich | ≥ 99.0 % |
| Ethyl acetate | Sigma-Aldrich | ≥ 99.5% |
| Hydrochloric acid | Sigma-Aldrich | puriss p.a., ≥ 37 % |
| Hydrofluoric acid | AnalaR NORMAPUR | 40 % |
| Hydroxylammonium chloride | Riedel-de-Haën | ≥ 99.0 % |
| Methyl isobutyl ketone | Sigma-Aldrich | ≥ 99.0 % |
| Nitric acid | Sigma-Aldrich | puriss p.a., ≥ 65 % |
| Oxalic acid dehydrate | Sigma-Aldrich | ≥ 99.0 % |
| Sodium hydrosulfide monohydrate | Sigma-Aldrich | ≥ 90.0 % |
| Sodium sulfide nonahydrate | Sigma-Aldrich | ≥ 98.0 % |
| Sulphuric acid | Sigma-Aldrich | puriss p.a., 95-97 % |
| Tributyl phosphate | Sigma-Aldrich | ≥ 97.0 % |
| Tri-n-octyl amine | Sigma-Aldrich | 98.0 % |

4.3 Instrumentation

The measurements were carried out with a PerkinElmer Optima 4300 DV ICP-OES equipped with an AS-90Plus Autosampler and a PerkinElmer Optima 8300 ICP-OES with a S10 Autosampler (Figure 3). The former instrument was used at the beginning of the study, mainly to determine the concentration from total digestion samples and samples from initial sequential extraction tests. The samples from later tests (oxalic acid extraction, sulfide precipitation, and liquid-liquid extraction) were measured by the Optima 8300 instrument (Fig. 3). A Scott type double-pass spray chamber equipped with a cross-flow nebulizer and cyclone spray chamber with a GemCone nebulizer were used. The element concentrations were determined using robust plasma conditions. Robust plasma was obtained by using the following conditions: nebulizer flow 0.6 l min⁻¹, auxiliary gas flow 0.2 l min⁻¹, plasma gas flow 8 l min⁻¹ (PerkinElmer Optima 8300) /15 l min⁻¹ (PerkinElmer Optima 4300 DV) and a plasma power of 1400 W or 1500 W. Axial measurement was used in the determination of Au, Ir, Pd and Pt while radial measurement was used in the determination of Co, Cr, Cu, Ni, V and Zn. The calibration for both instruments was carried out by using four-point

calibration. The concentrations of the standard solutions were 0; 0.08; 0.4 and 2 mg l⁻¹ and they contained a 20% (v/v) *aqua regia* as a background. A standard solution was measured before, between (every tenth sample), and after the measurement series to check the stability of the measurement.

An ultrasound water bath (ELMA, Model Transsonic 820/H, 650 W, 35 kHz) was utilized in sonication. A mechanical shaking equipment (Flask Shaker SF1, Stuart Scientific, UK) was used in the extractions. The samples were centrifugated by using Heraeus Instruments Megafuge 1.0 equipment. Carbon and nitrogen concentrations were determined with an Elementar Vario EL III analyzer, and pHs were measured at a L/S ratio of 2.5:1 (v/v)²⁰¹ using Orion 720A pH-meter equipment.

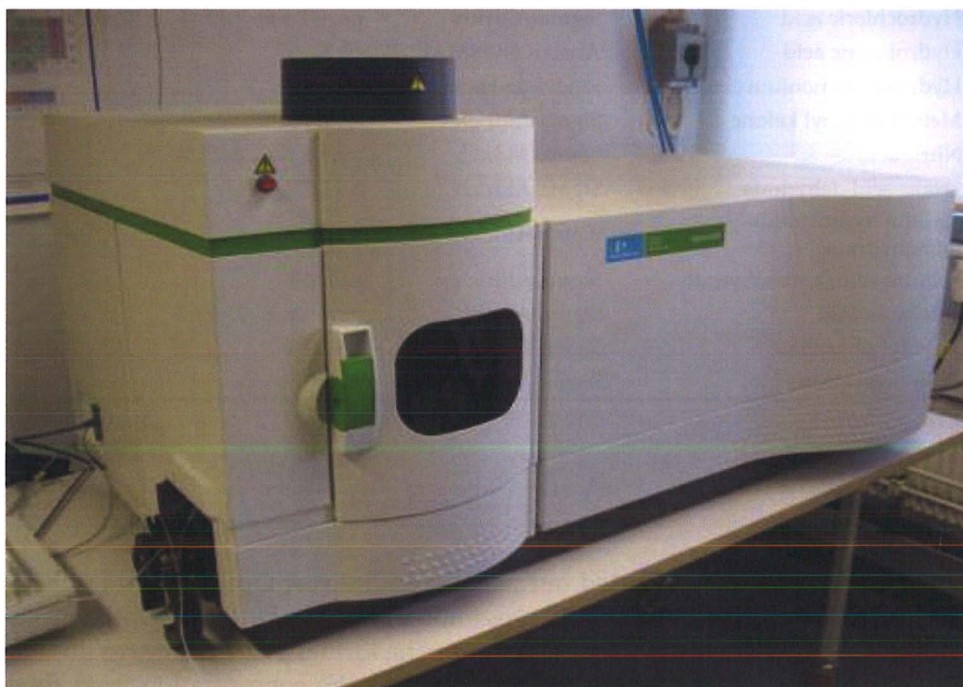


FIGURE 3 Inductively coupled plasma optical emission spectrometer (PerkinElmer Optima 8300).

4.4 Magnetic separation procedure

5 g of fly ash was accurately weighed onto a glass plate and spread into a thin layer. A bar magnet was moved over the ash. The magnetic and non-magnetic fraction were collected, weighed and digested according to the one-step ultrasound-assisted digestion procedure (4.5). The samples were filtered into a 100 ml volumetric flask and filled to the mark with water.

4.5 Ultrasound-assisted digestion procedures

An ash sample of 500 mg was accurately weighed into a 50 ml plastic screw-top centrifuge tube. The digestion solution was added and the tube was closed loosely and placed into an ultrasound water bath. Between the sonication periods the samples were shaken by hand to prevent sedimentation. The digestion procedures used were:

1. 8 ml of *aqua regia* + 0.3 ml of HF was added to the ash sample of 500 mg. The sample was sonicated for 9 min (3x3 min) in 60 °C after which the sample was filtered (Whatman 41) into a 50 ml volumetric flask and diluted to the mark with water. The residue was washed with 15 ml of water introduced in four portions. Finally the sample solution was transferred into a plastic screw-top bottle for storage.
2. Two-step ultrasound-assisted digestion was carried out according to Ilander and Väisänen's procedure.⁸⁸

In the first step 6 ml of HNO₃ was added to an ash sample of 250 mg. The sample was sonicated for 9 min (3x3 min) at 60° C after which the sample was centrifuged (Heraeus Instruments Megafuge 1.0, 2500 rpm) and the supernatant was separated from the residue with a pipette. In the second step the residue was digested using a digestion solution of 3 ml of HNO₃ + 3 ml of HF. After 18 minutes of sonication the sample solution was filtered into the same volumetric flask (100 ml) with the supernatant from the first step and diluted to the mark with water. The residue was washed with 15 ml of water introduced in four portions. Finally the sample solution was transferred into a plastic screw-top bottle for storage.

4.6 Digestion in an autoclave

To evaluate the efficiency of the ultrasound-assisted digestion a reference digestion method in autoclave, slightly modified from Medved *et al.*²⁰² was performed. A sample of about 250 mg was accurately weighed into a PTFE decomposition vessel into which 5 ml of HNO₃ and 2 ml of HF was added. The vessel was closed in an autoclave and heated at 160 °C for 4 h. After cooling, 10 ml of 10% (v/v) HCl and 5 ml of saturated H₃BO₃ was added. The sample was filtered (Whatman 41) into a 100 ml volumetric flask and diluted to the mark with water. The residue was washed with 15 ml of water introduced in four portions. Finally the sample solution was transferred into a plastic screw-top bottle for storage.

4.7 Sequential extraction procedures

The leaching behavior of elements was evaluated first by the conventional sequential extraction procedure with a total time of 22.5 h and the ultrasound-assisted sequential extraction procedure, slightly modified from Väisänen and Kiljunen¹⁴⁷ with a total time of 72 min (18+6+12+18+18 min) (Table 8).

4.7.1 Conventional sequential extraction procedure

A slightly modified procedure from the Tessier protocol¹⁴¹ was used. The reagents, extraction times and temperature used are presented in Table 8. 1000 mg of ash sample was accurately weighed into a 50 ml polypropylene centrifuge tube. Mechanical shaking equipment (Flask Shaker SF1, Stuart Scientific, UK) was utilized in the extraction steps i and ii and an ultrasonic water bath (ELMA, Model Transsonic 820/H, 650 W, 35 kHz) in order to heat samples in the extraction steps iii-v. Between the extraction steps the sample tubes were centrifuged and the residue was washed with 8 ml of water and then extracted with the next extraction solution. The washing solution was transferred into the same volumetric flask of 50 ml with the supernatant (steps i-iv). Then, 1 ml of HNO₃ was added to ensure their safe storage (steps i and ii). Finally, the sample solution was diluted to volume with water (steps i-iv).

TABLE 8 Reagents, extraction time and temperature used in conventional (CSE) and ultrasound-assisted (UASE) sequential extraction procedures.

| Step | Procedure | Reagents | pH | Time | T(°C) |
|------|-----------|--|----|---------|--------|
| | CSE | 8 ml of 1 mol l ⁻¹ NH ₄ Cl ^a | 7 | 1 h | 25 |
| | UASE | 8 ml of 0.5 mol l ⁻¹ NH ₄ Cl ^a | 7 | 6*3 min | 25 |
| ii | CSE | 8 ml of 1 mol l ⁻¹ NaCH ₃ COO ^a | 5 | 5 h | 25 |
| | UASE | 10 ml of 1 mol l ⁻¹ NH ₄ CH ₃ COO ^a | 5 | 2*3 min | 25 |
| iii | CSE | 20 ml of 0.04 mol l ⁻¹ NH ₂ OH*HCl ^b | 2 | 6 h | 85 |
| | UASE | 10 ml of 0.04 mol l ⁻¹ NH ₂ OH*HCl ^b | 2 | 4*3 min | 85 |
| iv | CSE | 3 ml of 0.02 mol l ⁻¹ HNO ₃ + 5 ml of 30 % H ₂ O ₂ ^b | 2 | 2 h | 85 |
| | | 3 ml of 30 % H ₂ O ₂ | | 3 h | 85 |
| | | Into the cooled sample an addition of 5 ml of 3.2 mol l ⁻¹ NH ₄ CH ₃ COO | | | |
| | UASE | 3 ml of 0.02 mol l ⁻¹ HNO ₃ + 10 ml of 15 % H ₂ O ₂ ^b | 2 | 6*3 min | 85 |
| | | washing of the residue by 5 ml of 3.2 mol l ⁻¹ NH ₄ CH ₃ COO | | | |
| v | CSE | 3 ml HNO ₃ + 3 ml HF | | 5.5 h | 60 |
| | UASE | 3 ml HNO ₃ + 3 ml HF | | 6*3 min | 60 |

^a adjustment of pH with CH₃COOH^b adjustment of pH with HNO₃

The residue from step iv was digested by 3 ml of HNO_3 + 3 ml HF at 60 °C for 5.5 h and the solution was filtered (Whatman 41) into a 100 ml plastic volumetric flask. The residue was washed with 15 ml of water introduced in four portions, and the filtrate was diluted to volume with water. Finally, the sample solution was transferred into a plastic screw-top bottle for storage.

4.7.2 Ultrasound-assisted sequential extraction procedure

1000 mg of ash sample was accurately weighed into a 50 ml polypropylene centrifuge tube and extracted by ultrasound in five stages in an otherwise similar manner to the conventional extraction. The temperature used was the same but the concentration of reagents (steps i-iv) and extraction times were different compared to the respective ones in conventional extraction (Table 8). After each extraction procedure, the sample solution was centrifuged (Heraeus Instruments Megafuge 1.0, 2500 rpm) and the solution was pipetted into a volumetric flask (25 or 50 ml). After centrifugation, the residue was washed with 8 ml of water (steps i-iii) or 5 ml of 3.2 mol l^{-1} $\text{NH}_4\text{CH}_3\text{COO}$ (fraction 4), which was centrifuged and pipetted into the same volumetric flask with the sample solution and filled to the mark with water.

4.8 Ultrasound-assisted extraction by oxalate reagents

The extraction was performed by using two sample weights, 1 g and 10 g. The same liquid-to-solid ratios were applied for both sample weights. The maximum temperatures of the water bath using centrifuge tubes and Erlenmeyer flasks as sample vessels were 85 °C and 75 °C, respectively.

Sample weight of 1 g¹⁸⁹

An ash sample of about 1 g was accurately weighed into a 50 ml centrifuge tube and 20 ml of 0.1-0.75 mol l^{-1} of ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$) or oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) was added. The pH of the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution was adjusted to 2 by HNO_3 or HCl . Oxalic acid was used as such (pH 0.9) or at pH 1.5-2. The adjustment of the pH was carried out using NH_4OH . The sample was sonicated in two steps at 85 °C with the following contact times:

- i) 6 min (2x3 min)
- ii) 12 min (4x3 min).

Between the steps the sample was left to stand in a water bath for 30 min without sonication. After step ii the sample was centrifuged. Finally the liquid phase was separated from the residue by a pipette and transferred into a 50 ml volume flask and filled to the mark with water.

Sample weight 10 g

An ash sample of about 10 g was accurately weighed into a 500 ml Erlenmeyer flask and 200-250 ml of 0.35-0.85 mol l⁻¹ H₂C₂O₄ was added. The extraction was performed at 75 °C in three stages:

- i) 6 min (3+3 min)
- ii) 12 min (3+3+3+3 min)
- iii) 12 min (3+3+3+3 min).

Between the steps the sample was left to stand in a water bath for 30 min without sonication. The flasks were left overnight in fume cupboards to ensure the settling of the residue ash particles into the bottom of the flask. The liquid phase was separated from the residue by a pipette and transferred into a 250 ml volume flask. The residue was filtered into the same volume flask and was washed with 15 ml of water introduced in four portions. Finally, the sample solution was diluted to volume with water.

4.9 Sulfide precipitation procedure¹⁸⁹

To a 20 ml H₂C₂O₄ or (NH₄)₂C₂O₄ leachate obtained by ultrasound-assisted extraction (4.8) 1 ml of 0.5-0.7 mol l⁻¹ Na₂S and 1 ml of 2.3 - 2.7 mol l⁻¹ NH₄Cl solution was added. The pH of the solution was adjusted to 1.5±0.3 by HCl after which the solution was warmed at 60 °C with continuous stirring for 30 min. The cooled solution was centrifuged and the liquid phase was separated from the precipitate by pipette. The pH of the separated liquid phase was adjusted to 8.5±0.3 by NH₄OH where the second precipitate was formed.

4.10 Solvent extraction procedure

The pH of H₂C₂O₄ leachate obtained by ultrasound-assisted extraction (4.8) was adjusted to 0.8 by 5 mol l⁻¹ NH₄OH and standard addition of 1 mg l⁻¹ (Au, Ir, Pd, Pt) was performed. 20 ml of this solution was combined with 20 ml of Aliquat 336 (4%, in ethyl acetate) in an 100 ml Erlenmeyer flask. The flask was stirred continuously (230 rpm) for 2 h in an ambient temperature. The solution was transferred to a 100 ml separatory funnel. The phases were left to settle for 15 min after which the lower phase were released from the bottom of the separatory funnel. The back extraction was performed by combining the organic phase from the liquid-liquid extraction with 20 ml of solution which was 0.5 mol l⁻¹ respective to CH₄N₂S and HCl.

The flask was stirred continuously (230 rpm) for 2 h in an ambient temperature. The solution was transferred into a 100 ml separatory funnel. The phases were left to settle for 15 min after which the lower phase was released from the bottom of the separatory funnel and analyzed by ICP-OES.

5 RESULTS AND DISCUSSION

First, the concentrations of valuable elements (Au, Co, Cr, Cu, Ir, Ni, Pd, Pt, V, Zn) were determined from fly ash samples by ICP-OES using ultrasound-assisted digestion. Although the determination of other elements (Al, As, Ca, Fe, K, Mg, Mn, P, Pb, S, Si, Ti, W) was not in the scope of this work it was carried out in order to obtain more information about the chemical composition of the samples. This is due to their high concentrations in the sample matrix. Most of them can be regarded as easily ionized elements and they have significant effects on plasma robustness. They may also cause the spectral interferences on analyte elements. The method was validated by using the certified reference material SRM1633b (Coal Fly Ash). Unfortunately the SRM sample applied does not contain the noble metals investigated in this work. Due to this, the recovery test with the standard addition of noble metals at two levels of concentrations was performed using real fly ash samples. Secondly, a multiple linear regression model (MLR) was applied to correct the interferences caused by the matrix elements in the determination of the noble metals by ICP-OES. Thirdly, the leaching behavior of the aforementioned elements was evaluated by the ultrasound-assisted sequential extraction method. Fourthly, the ultrasound-assisted method for the leaching of valuable metals (Au, Co, Cr, Cu, Ir, Ni, Pd, Pt, V, Zn) from fly ash samples by oxalic acid was developed. Fifthly, in order to recover the noble metals from oxalic acid leachate of fly ash a sulfide precipitation and solvent extraction method was developed.

5.1 Calibration

The working range for the analysis of Co, Cr, Cu, Ni, V and Zn was 0 – 10.00 mg l⁻¹ while for Au, Ir, Pd and Pt it was 0 – 2.00 mg l⁻¹. A four-point calibration was performed before every measurement. Multi-element calibration standards for valuable metals (Co, Cr, Cu, Ni, V, Zn, Pd, Pt, Au, Ir) and matrix elements (Al, As, Ca, Fe, K, Mg, Mn, P, Pb, S, Si, Ti, W) were utilized. The limit of detection (LOD) and the limit of quantification (LOQ) was calculated by substituting ($y_b + 3s_b$) and ($y_b + 10s_b$) into the calibration line $y = bx + a$, respectively.⁶⁹

The calibration data is presented only for valuable metals and for W since even low concentrations of W interfered the determination of Au at 267.595 nm and Pt at 265.945 nm (Table 9). Excellent *r* values were obtained for every element and all LOQs obtained resulted in <0.07 mg l⁻¹. Typical RSD values of the ICP-OES instruments for each element were < 2.6 %.

TABLE 9 Calibration data for the determination of valuable metals by ICP-OES.

| Element | Wavelength (nm) | R | LOD (mg l ⁻¹) | LOQ (mg l ⁻¹) | Calibration ranges (mg l ⁻¹) |
|---------|-----------------|--------|---------------------------|---------------------------|--|
| Au | 267.595 Axial | 0.9999 | 0.019 | 0.064 | 0.08-2 |
| Co | 228.616 Radial | 0.9999 | 0.006 | 0.019 | 0.1-10 |
| Cr | 267.716 Radial | 0.9999 | 0.005 | 0.017 | 0.1-10 |
| Cu | 327.393 Radial | 1.0000 | 0.005 | 0.017 | 0.1-10 |
| Ir | 224.268 Axial | 0.9999 | 0.012 | 0.041 | 0.08-2 |
| Ni | 231.604 Radial | 1.0000 | 0.002 | 0.007 | 0.1-10 |
| Pd | 340.458 Axial | 0.9999 | 0.009 | 0.029 | 0.08-2 |
| Pt | 214.423 Axial | 1.0000 | 0.004 | 0.015 | 0.08-2 |
| Ti | 334.940 Axial | 0.9999 | 0.011 | 0.039 | 0.1-10 |
| V | 290.880 Radial | 0.9999 | 0.009 | 0.031 | 0.1-10 |
| W | 207.912 Axial | 0.9998 | 0.013 | 0.046 | 0.1-10 |
| Zn | 206.200 Radial | 1.0000 | 0.010 | 0.034 | 0.1-10 |

5.2 Magnetic separation of Co, Cr, Cu, Ni, V and Zn from fly ash

Since Co and Ni are ferromagnetic metals a feasibility of magnetic separation as a preconcentration method in a recovery of them and Cu, Cr, V and Zn from fly ash samples was studied. The portions of magnetic and non-magnetic fractions of fly ash were approximately 60% and 40% (m/m), respectively. The concentrations were determined from samples resulting from ultrasound-assisted digestion procedure. All metals investigated were slightly more concentrated in magnetic ash fraction than in original fly ash (Fig. 4). The mean concentrations of Co, Ni, Cr and V were over 140 % compared to respective mean concentrations in the original fly ash. However, magnetic separation of the

elements was not further studied in this work and the focus was set in the hydrometallurgical recovery methods.

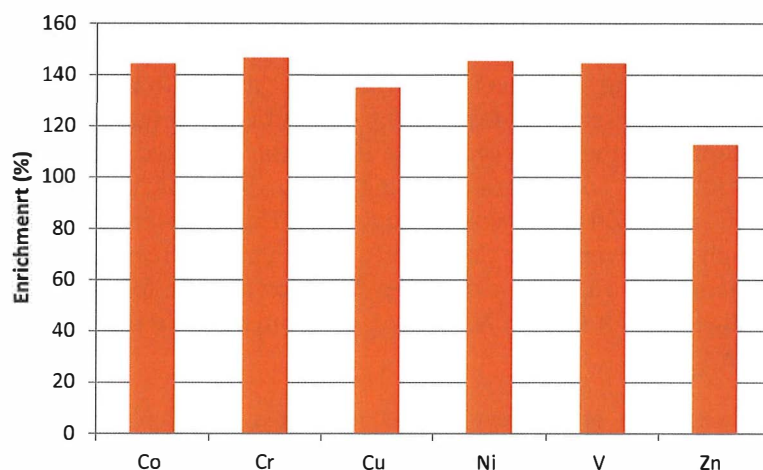


FIGURE 4 Co, Cr, Cu, Ni, V and Zn mean concentrations in magnetic fly ash fraction compared to respective mean concentrations in original fly ash sample (n=3).

5.3 Ultrasound-assisted digestion procedures

A two-step ultrasound-assisted nitric acid/hydrofluoric acid digestion reported by Ilander and Väisänen⁸⁸ was used. Additionally, a single-step procedure using *aqua regia* with HF as a digestion solution was also applied. The total digestion procedures were validated by using the standard reference material SRM1633b (Coal Fly Ash).

Comparison of two-step and one-step procedures

The ultrasound-assisted two-step digestion with a digestion solution of HNO₃ and HF at 25 °C and 60 °C was tested. The higher temperature used resulted in a higher recovery rate with trace elements except for Zn (Table 10). The recoveries of over 80% for the elements Cr, Cu and V were attained. All Co and 89.4% of Zn was dissolved. However, it should be noted that the concentrations of Co and Zn are not certified for SRM1633b.

Both *aqua regia* and (1+1) diluted *aqua regia* with HF were tested as a digestion solution. For the digestion of Cu one-step *aqua regia*/HF digestion was found to be more effective than two-step digestion (Table 10). The measured Cu concentration exceeded slightly the certified Cu concentration in SRM1633b. The measured concentration of Zn exceeded notably the certified Zn concentration in SRM1633b. Van Herreweghe *et al.*¹³¹ reported excessive recovery for Zn in SRM1633b when HCl/HNO₃/HF (2:1:1) digestion was used. On the other hand,

for the Zn concentration only a non-certified value is given for the reference material SRM1633b.²⁰⁰ The deviation of measured Cu and Zn concentrations from the certified concentrations may indicate contamination of glassware or in the instrument or a measurement interference. *Aqua regia* was more effective than the diluted *aqua regia* for the digesting of Co, Cr, Cu, Ni, V and Zn. Although HF is effective in digesting siliceous minerals, its use can lead to the precipitation of Cr as an insoluble chromyl fluoride (CrO_2F_2).²⁰³ But when it was used with a low, catalytic volume together with *aqua regia*, ultrasound-assisted digestion resulted in higher leachability of chromium. Single-step digestion resulted in higher recoveries of Cu and Zn than two-step digestion. The two-step digestion at 60 °C produced higher recoveries for Co, Cr, Ni and V than the digestion performed at an ambient temperature. Thus, a one-step digestion at 60 °C for Cu and Zn while a two-step digestion for Co, Cr, Ni and V is recommended in the analysis of total concentrations.

TABLE 10 Comparison of different ultrasound-assisted digestion procedures for the determination of Co, Cr, Cu, Ni, V and Zn. Mean concentrations and standard deviations (mg kg^{-1}) in SRM1633b (n=3).

| Element | one-step digestion | | two-step digestion | | Certified |
|---------|------------------------------------|--|---|---|-----------|
| | <i>aqua regia</i> +HF ^a | (1+1) <i>aqua regia</i> +HF ^b | HNO ₃ +HF (60 °C) ^c | HNO ₃ +HF (25 °C) ^d | |
| Co | 39.5±1,3 | 30±3 | 54±2 | 47.8±0.7 | (50) |
| Cr | 54.8±0.6 | 35±3 | 160±4 | 120±4 | 198.2±4.7 |
| Cu | 120±4 | 77±6 | 94.3±1.4 | 92±3 | 112.8±2.6 |
| Ni | 80±2 | 65±4 | 110±3 | 95±3 | 120.6±1,8 |
| V | 210±4 | 190±13 | 270±2 | 260±4 | 295.7±3.6 |
| Zn | 300±6 | 160±10 | 187.7±1.1 | 207±5 | (210) |

^a A sample of about 500 mg was digested for 9 min (3x3 min) in 60 °C. Reagents used: 8 ml *aqua regia* + 0.3 ml HF. Final volume 50 ml.

^b A sample of about 250 mg was digested for 9 min (3x3 min) in 60 °C. Reagents used: 5 ml water + 5 ml *aqua regia* + 0.3 ml HF. Final volume 50 ml.

^c A sample of about 250 mg was digested in 60 °C in two steps using sonication times and reagents of i) 9 min (3x3 min), 6 ml HNO₃ ii) 18 min (6x3 min), 3 ml HNO₃ + 3 ml HF. Final volume 100 ml.

^d Otherwise as in ^c but T= 25 °C.

5.4 Total element concentrations in real fly ash samples

The real fly ash samples investigated contained lower concentrations of Al, As, Cr, Fe, Si, V and Zn than standard reference material SRM1633b. The highest Au, Ir and Pt concentrations were detected from bark ash, wood/peat ash and wood roots ash. Thus, total element concentrations are presented only for these samples (Tables 11 and 12). The highest Pt concentration was determined from wood/peat ash, 6.0±1.1 mg kg^{-1} (Table 11). Au was detected only from wood/peat ash while Ir from bark ash and wood roots ash. Pd was not detected

from any ash sample investigated. The bark ash contained a notably higher Zn concentration than the ashes from co-combustion (sludge/peat, peat/coal ashes) investigated in this work (Table 11).

TABLE 11 Mean concentrations and standard deviations (mg kg^{-1}) of Au, Ir, Pd, Pt, Co, Cr, Cu, Ni, V and Zn in different fly ashes investigated ($n=3$).

| Element | Bark ash | Wood 80 %/peat 20 % | Wood roots | Finnish bio fly ashes [26][27][47][88][206][207] |
|-----------------|-------------------|------------------------|-------------------|---|
| Au ^a | <LOD ^d | 0.74±0.14 | <LOD ^d | |
| Ir ^a | 3.5±0.6 | <LOD ^f | 3.65±0.05 | |
| Pd ^a | <LOD ^e | <LOD ^e | <LOD ^e | |
| Pt ^a | 1.3±0.3 | 6.0±1.1 | <LOD ^g | |
| Co ^b | 3.3±0.2 | 5.0±0.3 | 5.70±0.04 | 8-16 |
| Cr ^b | 22±3 | 36±2 | 22±1 | 24-290 |
| Cu ^c | 75.2±1.2 | 81±4 | 163±1 | 60-483 |
| Ni ^b | 11±2 | 20.4±0.9 | 16.7±0.8 | 31-182 |
| V ^b | 6.0±0.3 | 68±4 | <LOD ^h | 39-168 |
| Zn ^c | 290±11 | 400±14 | 1200±50 | 275-3630 |

^a A sample of about 500 mg was digested for 9 min (3×3 min) in 60°C. Reagents used: 8 ml of *aqua regia* + 0.3 ml of HF. Final volume 50 ml.

^b A sample of about 250 mg was digested in 60 °C in two steps using sonication times and reagents of: i) 9 min (3×3 min), 6 ml of HNO₃ ii) 18 min (6×3 min), 3 ml of HNO₃+ 3 ml of HF. Final volume 100 ml.

^c Otherwise as in ^b but T= 25 °C.

^d LOD = 1.9 mg kg^{-1}

^e LOD = 0.9 mg kg^{-1}

^f LOD = 1.2 mg kg^{-1}

^g LOD = 0.4 mg kg^{-1}

^h LOD = 3.6 mg kg^{-1}

The Finnish fly ashes from the combustion of wood residue have been reported to contain, in addition to K, Mg, Mn and S, higher Cr, Cu, Mn, Ni, V and Zn concentrations than fly ashes from co-combustion of wood residue with peat and coal.^{88, 204}

It can be seen that the bark ash investigated in this work contained higher Ca, K, Mn, Ni, P and Zn concentrations while lower Al, As, Cr, Fe and Pb concentrations than in co-combustion ashes (Tables 11 and 12). The same was also reported in the works of Steenari *et al.*⁶¹ and Manskinen *et al.*^{39, 205} Sludge/peat fly ash contained the most Cu and Cr while peat/coal fly ash was richest in Co and V.

TABLE 12 Mean concentrations and standard deviations (mg kg⁻¹) of matrix elements in different fly ashes investigated (n=3).

| Element | Bark ash | Wood 80 %/peat 20 % ash | Wood roots ash | Finnish bio fly ashes [26][27][47][88][204][205] |
|---------------------------------------|-----------|-------------------------------|-------------------|---|
| Major elements (g kg ⁻¹) | | | | |
| Al ^a | 20.0±0.4 | 55.0±1.6 | 10.0±0.7 | 22.9-27.7 |
| Ca ^a | 212±4 | 100±4 | 200±10 | 62.3-173.0 |
| Fe ^b | 6.0±0.5 | 100.0±1.2 | 1.50±0.11 | 13.2-85.7 |
| K ^a | 30.0±0.8 | 11.0±0.6 | 46.0±1.5 | 4.2-65.0 |
| Mg ^a | 21.0±0.5 | 9.1±0.3 | 22.0±0.7 | 1.9-19.4 |
| Mn ^b | 7.3±0.2 | 3.80±0.15 | 9.0±0.4 | 0.52-20.00 |
| P ^b | 13.0±0.3 | 8.0±0.4 | 13.2±0.12 | 0.6-10.0 |
| S ^b | 2.59±0.13 | 5.2±0.2 | 3.39±0.08 | 4.7-24.1 |
| Sj ^b | 19±2 | 26±5 | 13.0±0.8 | 64.9 |
| Trace elements (mg kg ⁻¹) | | | | |
| As ^c | 4.2±1.1 | 25.7±1.3 | 3.9±0.5 | <57 |
| Pb ^b | 12±2 | 18.0±1.1 | 16±2 | 31-182 |
| Ti ^c | 250±30 | 620±30 | 230±12 | 250-840 |
| W ^c | 13.1±0,6 | 5.5±0.3 | 1.47±0.14 | |

^a A sample of about 250 mg was digested in 25 °C in two steps using sonication times and reagents of: i) 9 min (3x3 min), 6 ml of HNO₃ ii) 18 min (6x3 min), 3 ml of HNO₃+ 3 ml of HF. Final volume 100 ml.

^b Otherwise than in a but T = 60 °C.

^c A sample of about 250 mg was digested in 60 °C in two steps using sonication times and reagents of: i) 9 min (3x3 min), 6 ml of HNO₃ ii) 18 min (6x3 min), 3 ml of HNO₃+ 3 ml of HF. Final volume 100 ml.

5.5 The determination of Au, Ir, Pd and Pt by ICP-OES

The spectral interferences of Au, Ir, Pd and Pt were investigated carefully. Two requirements for the analytical lines of Au, Ir, Pd and Pt were set. First, the line should be as least affected by the emission of the matrix elements as possible. Secondly, the line should be sensitive so that emission line of the analyte can be distinguished from the emission of the matrix elements. The investigated lines are presented in Table 13.

TABLE 13 The investigated lines in determination of Au, Ir, Pd and Pt by ICP-OES.

| Analyte | Line (nm) | | |
|---------|-----------|---------|---------|
| Au | 208.209 | 242.795 | 267.595 |
| Ir | 205.222 | 224.268 | |
| Pd | 324.270 | 340.458 | 363.470 |
| Pt | 204.937 | 214.423 | 265.945 |

5.5.1 Initial interferences observed

The recovery test was carried out using two different ash total digestion samples (Table 14). The test was performed by adding the standard solution to samples at two levels of concentrations, 0.1 and 0.2 mg l⁻¹. For both samples the following procedure was used: a one-step ultrasound-assisted digestion procedure (4.5) was applied to six replicate samples and the samples were prepared into a volume of 50 ml. The samples were diluted (1+1) and into samples 1 and 2 no addition, into samples 3 and 4 an addition of 0.1 mg l⁻¹ and into samples 5 and 6 an addition of 0.2 mg l⁻¹ was performed before filling to mark with water. The mean concentrations of samples 1 and 2; 3 and 4; 5 and 6 were calculated. The measured concentration was calculated as follows:

$$\text{addition of 0.1 mg l}^{-1}: \text{mean (3 and 4) - mean (1 and 2)} \quad (10)$$

$$\text{addition of 0.2 mg l}^{-1}: \text{mean (5 and 6) - mean (1 and 2)} \quad (11)$$

The recoveries were calculated as follows:

$$\text{addition of 0.1 mg l}^{-1}: \text{measured concentration calculated by eq. 10} / 0.1 \text{ mg l}^{-1} \quad (12)$$

$$\text{addition of 0.2 mg l}^{-1}: \text{measured concentration calculated by eq. 11} / 0.2 \text{ mg l}^{-1} / 0.2 \text{ mg l}^{-1} \quad (13)$$

With the exception of Ir in peat/coal ash, the addition of 0.2 mg l⁻¹ of every element was measured with better recovery than with the addition of 0.1 mg l⁻¹. With the exception of Ir in bark ash (addition 0.2 mg l⁻¹) and in peat/coal ash (addition 0.1 mg l⁻¹) and Pt in bark ash (addition 0.1 mg l⁻¹) the recoveries resulted in lower than 90%.

TABLE 14 Results of the recovery test. Added concentrations (AC, mg l⁻¹) and recovery (Rec., %)

| Analyte line (nm) | Bark ash | | | | Peat/coal ash | | | |
|-------------------|----------|----------|-------|----------|---------------|----------|-------|----------|
| | AC | Rec. (%) | AC | Rec. (%) | AC | Rec. (%) | AC | Rec. (%) |
| Pt 214.423 | 0.100 | 89.4 | 0.200 | 92.5 | 0.100 | 82.3 | 0.200 | 87.8 |
| Pd 340.458 | 0.100 | 50.9 | 0.200 | 75.1 | 0.100 | 57.0 | 0.200 | 74.5 |
| Au 267.595 | 0.100 | 71.3 | 0.200 | 86.0 | 0.100 | 65.2 | 0.200 | 81.7 |
| Ir 224.268 | 0.100 | 29.4 | 0.200 | 139.5 | 0.100 | 92.3 | 0.200 | 64.5 |

A series of synthetic samples containing the analytes (Au, Ir, Pd, Pt) in tandem with the matrix elements (B, Co, Cr, Cu, Fe, Ge, Mn, Mo, Nb, Ni, P, Re, S, Si, Ta, Ti, W, Zr) were measured and the interfering lines identified. This was performed by using the spectrum library of Winlab software used in the PerkinElmer Optima 8300. The spectral interference of Cu 224.262 nm on line Ir 224.268 nm, Mn 242.795 nm on line Au 242.798 nm and Fe on line Pd 363.470 nm, reported earlier in the works of Torgov *et al.*¹⁰⁰, Malhotra *et al.*¹⁰¹ and Petrova *et al.*⁹⁸, respectively, were observed. Additionally, the interference from W on the

lines Pt 265.945 nm and Au 267.595 nm was observed. Next, synthetic solutions containing a) all the analytes and b) all the analytes and one matrix element (Si, Fe, Al, Cu, W) with a typical concentration in oxalic acid leachate were measured (Table 15). The added concentration of Au, Ir, Pd and Pt in solutions was 0.2 mg l^{-1} except in one synthetic solution (number 6) where by accident the addition of 0.4 mg l^{-1} was performed.

TABLE 15 Interferences in the determination of Au, Ir, Pd and Pt by ICP-OES. Measured concentrations (mg l^{-1}).

| Element | λ (nm) | Synthetic solution/concentration of interferent | | | | | |
|---------|----------------|---|-------------------------------|-------------------------------|-------------------------------|------------------------------|----------------------------|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| | | - | Si 600 mg l^{-1} | Fe 600 mg l^{-1} | Al 400 mg l^{-1} | Cu 20 mg l^{-1} | W 2 mg l^{-1} |
| Au | 242.795 | 0.205 | 0.213 | 0.173 | 0.192 | 0.207 | 0.371 |
| Au | 267.595 | 0.202 | 0.196 | 0.219 | 0.190 | 0.201 | 2.092 |
| Ir | 224.268 | 0.206 | 0.218 | 0.145 | 0.184 | 2.611 | 0.417 |
| Pd | 340.458 | 0.208 | 0.21 | 0.215 | 0.204 | 0.203 | 0.416 |
| Pd | 363.47 | 0.207 | 0.23 | 0.978 | 0.215 | 0.206 | 0.394 |
| Pt | 214.423 | 0.209 | 0.189 | 0.171 | 0.183 | 0.199 | 0.354 |
| Pt | 265.945 | 0.204 | 0.177 | 0.191 | 0.159 | 0.195 | 0.729 |

As also observed by Petrova *et al.*⁹⁸, the line Pd 363.470 nm was highly interfered with line Fe 363.469 nm (Table 15). Its emission was also increased by 15% due to the emission of Si. The line Pd 363.470 nm is not recommended since it is interfered with by the Ar 363.447 nm line.¹⁰¹ The emission signal using the line Pd 340.458 nm was slightly increased due to the emission of Si, Fe and W. Roy and Mistry⁹⁹ reported that from the solution containing Pd and Fe with concentrations of 1 mg l⁻¹ and 1000 mg l⁻¹, the measured Pd concentration of 1.2 mg l⁻¹ at line Pd 340.458 nm was determined. The interferences of lines Fe 340.436⁹⁸, Fe 340.44¹²² and W 340.53¹²² nm on this line have been reported earlier.

The intensity of line Pt 214.423 nm decreased due to the emission of all the matrix elements investigated except Cu. Malhotra *et al.*¹⁰¹ reported an interference of 0.23% on the intensity of this line while [Cu]:[Pt] was 10:1 in the synthetic sample solution. Especially, W and Fe had the highest effect on Pt 214.423 nm. The interferences on the emission lines of Al 214.539^{98, 122}, Fe 214.390⁹⁸, Fe 214.445^{98, 122} and Fe 214.52 nm¹²² on this line nm have been reported earlier. Roy and Mistry⁹⁹ reported the opposite effect of Fe on this line. The emission of Fe (1000 mg l⁻¹) increased the intensity of line Pt 214.423 nm by 40%. The intensity of the line Pt 265.945 nm was highly increased when W was present with a concentration of 2 mg l⁻¹ in the solution.

The emission of Si increased the intensity of line Au 242.795 nm while it decreased the signal of the Au 267.595 nm line (Table 15). For both lines, the decrease in emission due to the emission of Al was observed. The emission of W and Fe increased the emission intensity of Au 267.595 nm but not that of Au 242.795 nm. Usually, the measured concentrations of Fe in H₂C₂O₄ leachates result in the range of 300-500 mg l⁻¹ implying problems in using the line of Au 267.595 nm. Fortunately, from H₂C₂O₄ leachate concentrations of less than 1 mg l⁻¹ for W were detected. The Au 242.795 line was highly interfered with by Mn 242.798 nm which has been reported earlier^{101, 105, 106, 118}. Au 208.209 nm was discarded as too high concentrations were obtained.

In the case of Ir only the emission line of 224.268 nm gave an emission intensity that could be distinguished from the emission of the background elements. The line of Cu 224.262 nm increased notably the signal of line Ir 224.268 nm. When the [Cu]:[Ir] was 100:1 in the synthetic solution the determined Ir concentration was over 10-fold higher than the real concentration (Table 15). In H₂C₂O₄ leachates the determined concentration of copper on average was < 1 mg l⁻¹ but in one sulfide precipitate sample (pH 1.5) the maximum concentration determined was 16 mg l⁻¹. Additionally, the emission of Fe and Al decreased while that of Si and W increased the emission of Ir 224.268 nm. Of the interferences observed the interference from lines Cu 224.262 nm^{100, 122} and Fe 224.18 nm¹²² has been reported earlier. Before the measurement of the H₂C₂O₄ leachate and dissolved sulfide precipitate samples the calibration was carried out using standards which contained all the background elements causing interference. However, the spectral interference caused by matrix elements was not totally eliminated. Thus, in the next step, a multiple linear regression

technique was tested in the correction of the interferences for the accurate determination of Au, Ir, Pd and Pt.

5.5.2 Multiple linear regression (MLR) model

A total of 28 synthetic sample solutions with both the concentrations of analytes (Au, Ir, Pd, Pt) and interferences (Cu, Fe, Mn, Si, Ti) at five levels of concentrations were prepared and measured by ICP-OES. Earlier knowledge of the concentration of the elements in oxalic acid leachate samples was utilized to decide the selected concentration ranges. The concentration ranges were produced in order to introduce one level lower and higher than the concentrations determined in oxalic acid leachates.

TABLE 16 Added (AC), measured (MC) and corrected (CC) concentrations (mg l⁻¹) of Au 267.595 nm and Ir 224.268 nm for matrix samples 1-28.

| Sample | Au 267.595 nm | | | Ir 224.268 nm | | |
|--------|---------------|-------|-------|---------------|-------|-------|
| | AC | MC | CC | AC | MC | CC |
| 1 | 0.040 | 0.096 | 0.068 | 0.080 | 0.397 | 0.085 |
| 2 | 0.040 | 0.072 | 0.062 | 0.240 | 0.392 | 0.242 |
| 3 | 0.160 | 0.175 | 0.170 | 0.400 | 0.646 | 0.408 |
| 4 | 0.040 | 0.076 | 0.052 | 0.400 | 0.706 | 0.399 |
| 5 | 0.120 | 0.136 | 0.133 | 0.080 | 0.250 | 0.079 |
| 6 | 0.120 | 0.154 | 0.129 | 0.240 | 0.301 | 0.243 |
| 7 | 0.080 | 0.106 | 0.090 | 0.240 | 0.544 | 0.253 |
| 8 | 0.080 | 0.091 | 0.092 | 0.080 | 0.315 | 0.080 |
| 9 | 0.200 | 0.236 | 0.216 | 0.240 | 0.464 | 0.235 |
| 10 | 0.120 | 0.155 | 0.134 | 0.080 | 0.146 | 0.086 |
| 11 | 0.080 | 0.092 | 0.101 | 0.160 | 0.398 | 0.146 |
| 12 | 0.080 | 0.108 | 0.093 | 0.160 | 0.148 | 0.151 |
| 13 | 0.160 | 0.159 | 0.169 | 0.080 | 0.419 | 0.077 |
| 14 | 0.080 | 0.105 | 0.095 | 0.160 | 0.234 | 0.158 |
| 15 | 0.160 | 0.168 | 0.168 | 0.080 | 0.073 | 0.081 |
| 16 | 0.120 | 0.133 | 0.142 | 0.400 | 0.391 | 0.410 |
| 17 | 0.040 | 0.069 | 0.057 | 0.240 | 0.364 | 0.233 |
| 18 | 0.040 | <LOD | | 0.240 | 0.301 | 0.233 |
| 19 | 0.120 | 0.126 | 0.129 | 0.320 | 0.296 | 0.324 |
| 20 | 0.120 | 0.130 | 0.132 | 0.160 | 0.216 | 0.156 |
| 21 | 0.160 | 0.187 | 0.188 | 0.320 | 0.614 | 0.319 |
| 22 | 0.160 | 0.169 | 0.180 | 0.320 | 0.482 | 0.328 |
| 23 | 0.200 | 0.229 | 0.219 | 0.320 | 0.288 | 0.302 |
| 24 | 0.160 | 0.198 | 0.178 | 0.400 | 0.496 | 0.381 |
| 25 | 0.200 | 0.221 | 0.221 | 0.320 | 0.543 | 0.317 |
| 26 | 0.200 | 0.205 | 0.217 | 0.160 | 0.446 | 0.142 |
| 27 | 0.080 | 0.112 | 0.102 | 0.400 | 0.517 | 0.382 |
| 28 | 0.200 | 0.220 | 0.212 | 0.240 | 0.276 | 0.244 |

Concentration ranges of matrix elements in samples: Cu 0.2-4.2 mg l⁻¹, Fe 300-900 mg l⁻¹, Mn 6-30 mg l⁻¹, Si 100-580 mg l⁻¹, Ti 2-34 mg l⁻¹.

In every sample the measured concentrations of Au (with the exception of sample 18, Table 16) and Pt were higher than the added concentrations (Table 17). In samples 16 and 20 the measured concentrations of Pd were <LOD (Table 17).

TABLE 17 Added (AC), measured (MC) and corrected (CC) concentrations (mg l⁻¹) of Pd 340.458 nm and Pt 214.423 nm for matrix samples 1-28.

| Sample | Pd 340.458 nm | | | Pt 214.423 nm | | |
|--------|---------------|-------|-------|---------------|-------|-------|
| | AC | MC | CC | AC | MC | CC |
| 1 | 0.150 | 0.131 | 0.151 | 0.450 | 0.469 | 0.462 |
| 2 | 0.250 | 0.254 | 0.252 | 0.150 | 0.237 | 0.160 |
| 3 | 0.150 | 0.160 | 0.148 | 0.350 | 0.384 | 0.353 |
| 4 | 0.250 | 0.258 | 0.256 | 0.250 | 0.270 | 0.258 |
| 5 | 0.200 | 0.202 | 0.198 | 0.050 | 0.112 | 0.053 |
| 6 | 0.200 | 0.156 | 0.205 | 0.350 | 0.369 | 0.359 |
| 7 | 0.100 | 0.092 | 0.101 | 0.150 | 0.241 | 0.164 |
| 8 | 0.050 | 0.014 | 0.051 | 0.050 | 0.132 | 0.051 |
| 9 | 0.100 | 0.126 | 0.097 | 0.150 | 0.190 | 0.155 |
| 10 | 0.050 | 0.059 | 0.052 | 0.350 | 0.421 | 0.348 |
| 11 | 0.200 | 0.179 | 0.194 | 0.250 | 0.314 | 0.260 |
| 12 | 0.050 | 0.037 | 0.048 | 0.250 | 0.271 | 0.260 |
| 13 | 0.150 | 0.137 | 0.144 | 0.450 | 0.476 | 0.447 |
| 14 | 0.150 | 0.095 | 0.149 | 0.250 | 0.268 | 0.256 |
| 15 | 0.250 | 0.223 | 0.254 | 0.350 | 0.406 | 0.354 |
| 16 | 0.050 | <LOD | | 0.450 | 0.512 | 0.462 |
| 17 | 0.150 | 0.115 | 0.151 | 0.150 | 0.231 | 0.153 |
| 18 | 0.200 | 0.161 | 0.202 | 0.450 | 0.556 | 0.464 |
| 19 | 0.200 | 0.181 | 0.198 | 0.150 | 0.261 | 0.162 |
| 20 | 0.050 | <LOD | | 0.050 | 0.140 | 0.060 |
| 21 | 0.150 | 0.125 | 0.150 | 0.250 | 0.349 | 0.252 |
| 22 | 0.200 | 0.154 | 0.201 | 0.050 | 0.100 | 0.063 |
| 23 | 0.100 | 0.118 | 0.098 | 0.050 | 0.088 | 0.051 |
| 24 | 0.250 | 0.186 | 0.237 | 0.050 | 0.114 | 0.055 |
| 25 | 0.100 | 0.047 | 0.097 | 0.250 | 0.284 | 0.251 |
| 26 | 0.100 | 0.044 | 0.103 | 0.350 | 0.453 | 0.359 |
| 27 | 0.050 | 0.056 | 0.049 | 0.450 | 0.504 | 0.454 |
| 28 | 0.250 | 0.185 | 0.245 | 0.450 | 0.546 | 0.454 |

Concentration ranges of matrix elements in samples: Cu 0.2-4.2 mg l⁻¹, Fe 300-900 mg l⁻¹, Mn 6-30 mg l⁻¹, Si 100-580 mg l⁻¹, Ti 2-34 mg l⁻¹.

The data was used to calculate the MLR model on a spreadsheet. The added concentration of analyte was selected as a dependent variable while the measured concentration of the analyte and the added concentration of the interferences were selected as non-dependent variables. All the non-dependent variables where regression with dependent variable were statistically significant ($p < 0.05$) were included in the multiple expression line (Table 20). After the correction by the multiple linear regression line no differences between the added and corrected concentrations in lines Pd 340.458 nm and Ir 224.268 nm were found using the paired t-test at $p < 0.05$ (Tables 18 and 19). The corrected

concentrations at Pt 214.423 nm are extremely near the added concentrations of Pt while all corrected concentrations at Au 267.595 nm are higher than the added Au concentrations. Thus, the use of the paired t-test for line Au 267.595 nm was not enabled.

TABLE 18 The results of t-test for lines Au 267.595 nm and Ir 224.268 nm calculated from data in Table 16. The unit for AC and MC is mg l⁻¹.

| Statistical parameter | Au 267.595 nm | | | | Ir 224.268 nm | | | |
|-----------------------|---------------|-------|-------|-------|---------------|-------|-------|-------|
| | AC | MC | AC | CC | AC | MC | AC | CC |
| Mean | 0.123 | 0.145 | 0.123 | 0.139 | 0.234 | 0.381 | 0.234 | 0.232 |
| Variance | 0.003 | 0.003 | 0.003 | 0.003 | 0.013 | 0.024 | 0.013 | 0.013 |
| n | 27 | 27 | 27 | 27 | 28 | 28 | 28 | 28 |
| [t] | | | | | 6.53 | | 1.403 | |
| t _{crit} | | | | | 2.052 | | 2.052 | |

AC = added, MC = measured, CC = corrected concentration (mg l⁻¹)

TABLE 19 The results of t-test for lines Pt 214.423 nm and Au 267.595 nm calculated from data in Table 17. The unit for AC and MC is mg l⁻¹.

| Statistical parameter | Pd 340.458 nm | | | | Pt 214.423 nm | | | |
|-----------------------|---------------|-------|-------|-------|---------------|-------|-------|-------|
| | AC | MC | AC | CC | AC | MC | AC | CC |
| Mean | 0.156 | 0.134 | 0.156 | 0.155 | 0.25 | 0.311 | 0.25 | 0.256 |
| Variance | 0.005 | 0.004 | 0.005 | 0.005 | 0.021 | 0.021 | 0.021 | 0.022 |
| n | 26 | 26 | 26 | 26 | 28 | 28 | 27 | 27 |
| [t] | 4.101 | | 0.993 | | | | 7.001 | |
| t _{crit} | 2.06 | | 2.06 | | | | 2.052 | |

AC = added, MC = measured, CC = corrected concentration (mg l⁻¹)

From multiple linear regression expression equations it can be seen that all the regression correlation coefficients obtained were over 0.99. The line Pt 214.423 nm can be considered excellent in the determination of Pt from fly ash samples with r of 0.999. The spectral interference of Ti ($2.217 \cdot 10^{-3}$) and Cu ($1.653 \cdot 10^{-3}$) and on the signal at line Pd 340.458 nm are the second and third highest interferences observed. On the other hand, while the determined Cu concentrations in oxalic acid leachate were at levels of a few mg l⁻¹, the Fe concentration was between 300-900 mg l⁻¹ in all samples. Thus, the net interference of Fe on signals at analytical lines is also notable.

TABLE 20 Multiple linear regression expression and correlation coefficient, R, of Au 267.595 nm, Ir 224.268 nm, Pd 340.458 nm and Pt 214.423 nm.

| Analyte line | Multiple linear regression expression | R |
|---------------|--|-------|
| Au 267.595 nm | $[1.04498 \cdot \text{Au}] + [3.8100 \cdot 10^{-4} \cdot \text{Mn}] - [4.8760 \cdot 10^{-5} \cdot \text{Fe}] + [3.0089 \cdot 10^{-5} \cdot \text{Si}] - 0.01288$ | 0.990 |
| Ir 224.268 nm | $[1.0653 \cdot \text{Ir}] - [0.08725 \cdot \text{Cu}] + [4.6915 \cdot 10^{-5} \cdot \text{Fe}] + [5.9200 \cdot 10^{-4} \cdot \text{Ti}] + [4.2880 \cdot 10^{-5} \cdot \text{Si}] - 0.0327$ | 0.994 |
| Pd 340.458 nm | $[1.0728 \cdot \text{Pd}] - [1.6530 \cdot 10^{-3} \cdot \text{Cu}] - [3.2300 \cdot 10^{-5} \cdot \text{Fe}] + [2.2172 \cdot 10^{-3} \cdot \text{Ti}] + [2.7730 \cdot 10^{-5} \cdot \text{Si}] - 0.01458$ | 0.997 |
| Pt 214.423 nm | $[1.0240 \cdot \text{Pt}] - [1.8160 \cdot 10^{-4} \cdot \text{Si}]$ | 0.999 |

The emission of Mn and Si decreased the signal of Au 267.595 nm while the emission of Fe, as reported earlier¹⁰⁷, increased it (Table 21). The emission of line Cu 224.262 nm significantly increased the signal of Ir 224.268 nm, also reported earlier.¹⁰⁰ The emission of Fe, Ti and Si decreased the signal of Ir. With the exception of Fe, the signals of Cu, Ti and Si influenced the signal of Pd 340.458 nm in the same way. The Pd 340.458 nm line was found to be interfered with by the emission of Cu, Fe, Ti and Si. Interfering lines Fe 340.476 nm⁹⁸, Ti 340.337 nm⁹⁸ and Ti 340.50 nm¹²² have been reported earlier. The only interference on the signal of Pt was from the emission of Si which resulted in a slight increase of the emission of the analytical line. The spectral interferences observed in this work in tandem with the ones reported in the literature are presented in Table 21.

TABLE 21 Spectral interferences for lines Au 242.795, Au 267.595, Ir 224.268, Pd 340.458, Pt 214.423 and 265.945 nm by ICP-OES observed in this work and in earlier works.

| Analyte line (nm) | Interference found in this work | Interference earlier in Ref. |
|-------------------|---------------------------------|------------------------------|
| Au 242.795 | Fe (+) | [100][107][122] |
| | Mn 242.798 (+) | [101][106][107] |
| Au 267.595 | Fe(+) | [107] |
| | Mn(-), Si(-), W(+) | |
| Ir 224.268 | Cu 224.262(+) | [100] |
| | Fe(-), Ti(-), Si(-) | |
| Pd 340.458 | Cu(+), Fe(+), Ti(-), Si(-) | [98] |
| | Fe I 340.436 | [98][122] |
| Pt 214.423 | Fe (-), Al (-), | [98][122] |
| | | |
| Pt 265.945 | W (+) | |
| | Fe 265.924 | [98] |

+ = causes an increase on emission signal of analyte

- = causes a decrease on the emission signal of analyte

5.5.3 Recovery test for precipitate samples

The MLR model (5.5.2) was applied in the determination of Au, Ir, Pd and Pt from sulfide precipitate samples. The optimization of the sulfide precipitation procedure is presented in the section 5.7. Precipitate pH 1.5 and 8.5 refer to precipitate samples obtained at pH 1.5 and 8.5, respectively.

The precipitate pH 1.5 and 8.5 samples obtained after performing the optimized precipitation procedure (4.9) were dissolved in (1+1) *aqua regia* after which an addition of 0.08 or 0.4 mg l⁻¹ of precious element standard was performed and the flasks were filled to the mark with water. The calibration solutions were matrix matched with the sample solutions. In the precipitate pH 1.5 sample the recoveries were between 91.5-105.7% for Au, Pd and Pt with both standard additions and 95.8% for Ir with a standard addition of 0.4 mg l⁻¹ (Table 22). In the precipitate pH 8.5 sample the recoveries of between 95.0-108.8% for Au, Ir and Pd (standard addition of 0.08 mg l⁻¹) and 98.3% for Pt (standard addition of 0.4 mg l⁻¹) were obtained.

TABLE 22 Recovery test for sulfide precipitate pH 1.5 and 8.5 samples. Added concentration (AC) of the standard solution to dissolved precipitate samples. MC = measured concentration (mg l⁻¹). Rec. = recovery (%).

| Line (nm) | Precipitate pH 1.5 | | | | Precipitate pH 8.5 | | | |
|---------------|-----------------------------|-------|-----------------------------|-------|-----------------------------|-------|-----------------------------|------|
| | AC 0.08 mg l ⁻¹ | | AC 0.4 mg l ⁻¹ | | AC 0.08 mg l ⁻¹ | | AC 0.4 mg l ⁻¹ | |
| | MC (mg l ⁻¹) | Rec. | MC (mg l ⁻¹) | Rec. | MC (mg l ⁻¹) | Rec. | MC (mg l ⁻¹) | Rec. |
| Au 267.595 | 0.083 | 103.8 | 0.366 | 91.5 | 0.076 | 95.0 | 0.342 | 85.5 |
| Ir 224.268 | 0.064 | 80.0 | 0.383 | 95.8 | 0.077 | 96.3 | 0.358 | 89.5 |
| Pd 340.458 | 0.082 | 102.5 | 0.421 | 92.5 | 0.087 | 108.8 | 0.261 | 65.3 |
| Pt 214.423 | 0.078 | 97.5 | 0.423 | 105.7 | 0.069 | 86.3 | 0.393 | 98.3 |

5.6 Ultrasound-assisted sequential extraction of fly ash samples

5.6.1 Total leachable concentrations of Co, Cr, Cu, Ni, V and Zn

The elements Co, Cr, Cu, Ni, V and Zn can be regarded as sparsely soluble and are expected to show similar chemistry and thus similar leaching behavior to Au, Ir, Pd and Pt. In the periodic table of the elements Co is in group 9 together with Ir, Ni is in group 10 together with Pd and Pt while Cu is in group 11 together with Au. Thus, the leaching behaviour of them from the fly ash samples was investigated.

The ultrasound-assisted sequential extraction procedure by Väisänen and Kiljunen¹⁴⁷ was applied with the aim of shortening the extraction time of the

conventional extraction procedure. The certified reference material SRM1633b (Coal Fly Ash) and two different fly ash samples, bark ash and peat/coal fly ash, were extracted according to the optimized UASE procedure (4.7.2) and by the conventional sequential extraction procedure (4.7.1). Total leachable concentrations for both extracting methods were calculated by summing the concentrations obtained in each step of the extraction.

The 72 min UASE on SRM1633b (coal fly ash) resulted in two-fold higher total leachable concentrations of Fe and Al and 27% more of Mn than by the conventional extraction (time 22.5 h). This can be attributed to the effectiveness of sonication in digesting the reducible and residual fraction. 74-80% of Co, Cr, Cu, Ni, V and Zn were leached in the extraction while Pöykiö *et al.*²⁷ reported recoveries of over 87.7% for these elements. It should be noted that the results are not exactly comparable to our results as the leaching solutions and temperature used are different in the extraction protocols. They performed a non-accelerated 5-staged SE with a total time of 87 h on SRM1633b. In the scheme leaching was carried out by acidic water (pH 4.8) in step i, the steps ii-iv were carried out according to the original BCR protocol and in step v the residue from step iv was dissolved in a PTFE vessel by HNO₃, HCl and HF, in stepwise. For SRM1633b and peat/coal ash, no difference in the total leachable concentrations of Co, Cr, Cu, V and Zn obtained by ultrasound and conventional sequential extraction was observed (paired t-test, P = 0.05). Instead, Cr, Cu, V and Zn were leached better from bark ash by conventional sequential extraction. If comparable leached concentrations of Co, Cr, Cu, V and Zn can be obtained from fly ash with the time of 1/14 compared to the conventional sequential extraction protocol, performing the extraction using rapid, simple and safe UASE seems to be a method of choice.

The residual fraction of the sequential extraction contained high portions of Co, Cr, Cu, Ni, V and Zn. A major finding in this work was that while the oxide fraction of the ash dissolved a notable portion of these elements liberated into solution (Fig. 5 and 6). Additionally, it must be emphasized that after the combustion of the fuel the elements are mainly present as oxides in fly ash. Due to this, the focus of the work was set on the recovery of the valuable elements from the leachate obtained in the extraction of the oxide fraction. Thus, only the results from step iii, the oxide fraction, are reported in the rest of this chapter.

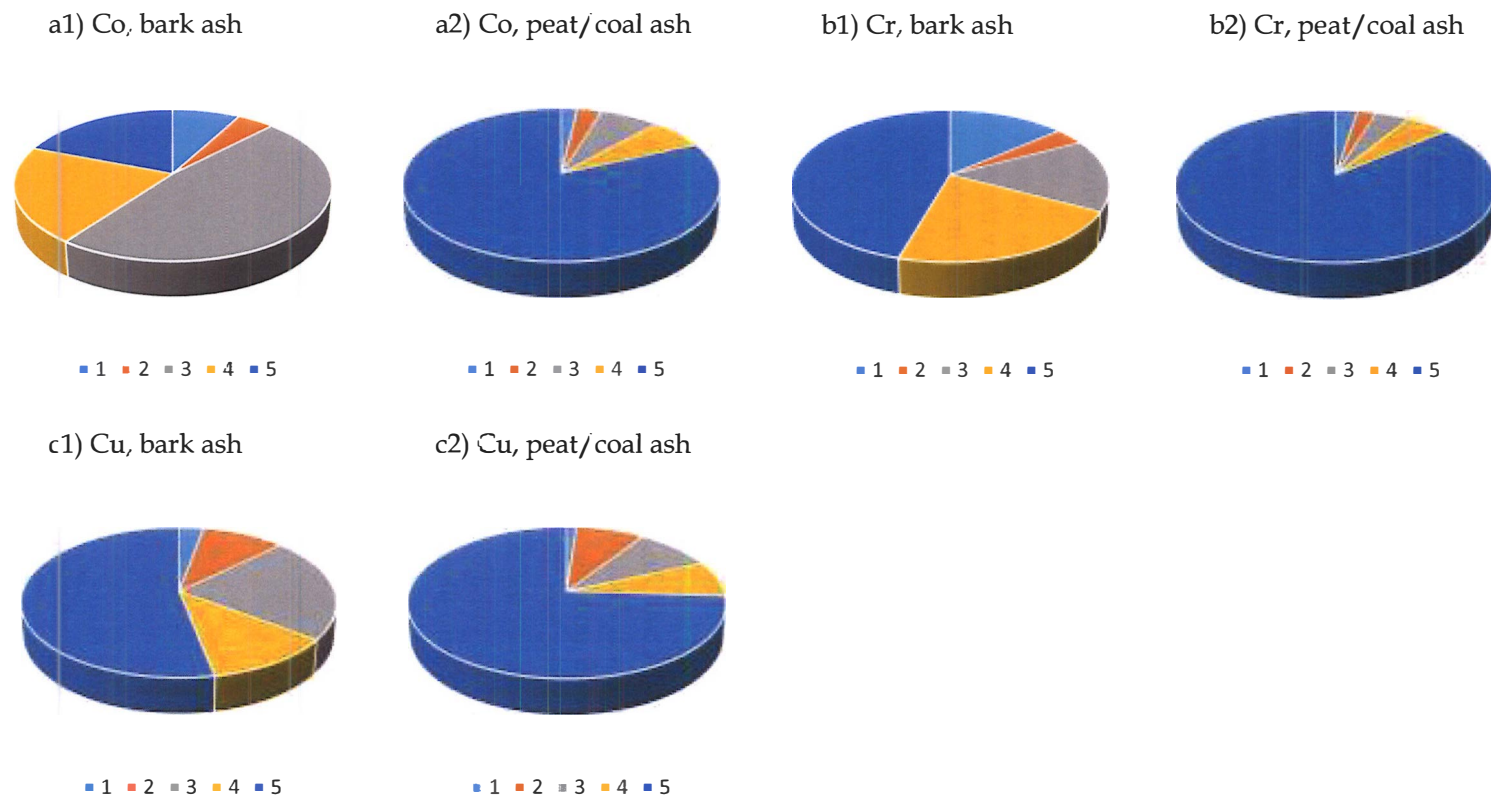


FIGURE 5 Percentage distribution of a) Co b) Cr and Cu between 1) exchangeable, 2) bound to carbonates, 3) bound to Fe-Mn oxides, 4) bound to organic matter and sulfides, and 5) a residual fraction. Samples: bark ash and peat/coal co-combustion ash.

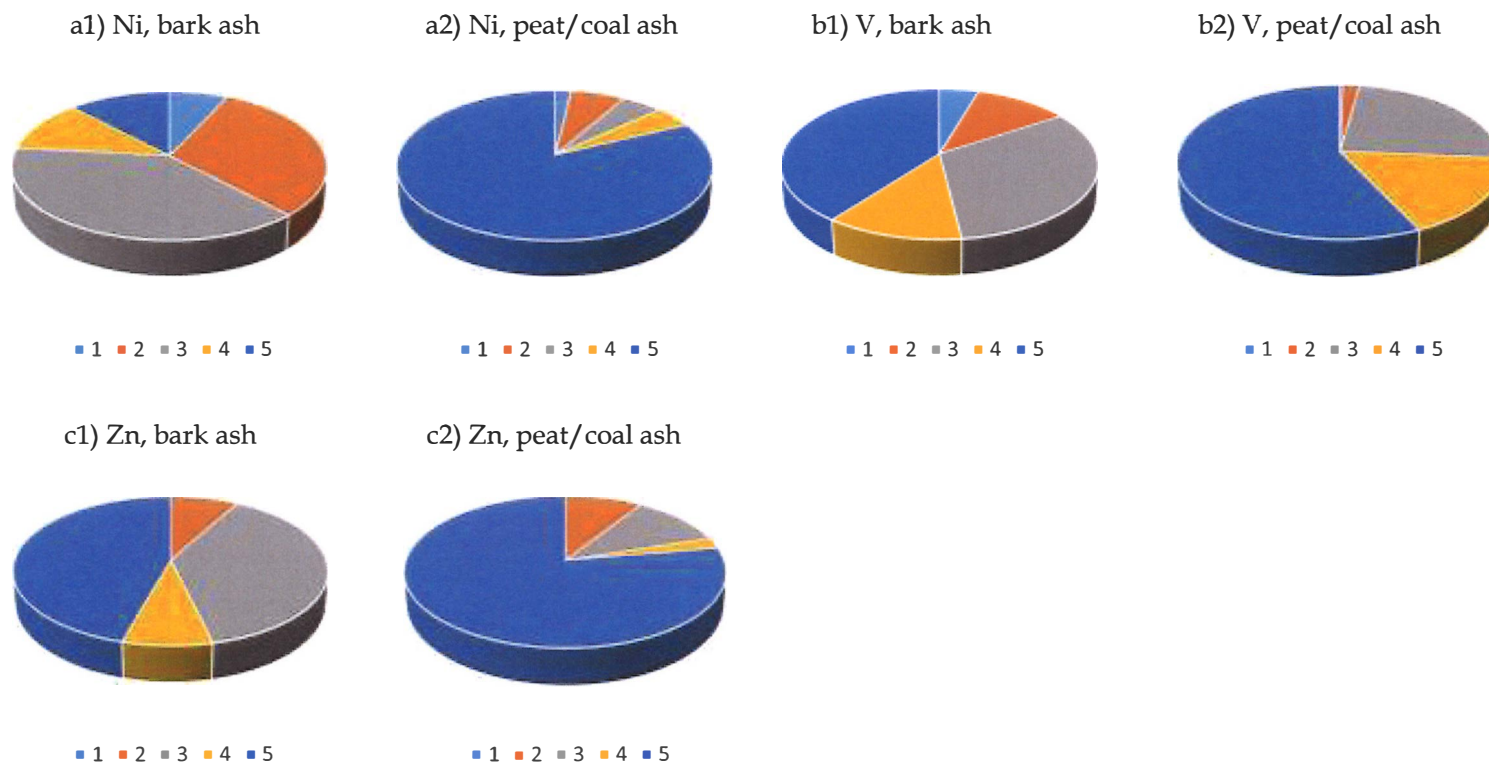


FIGURE 6 Percentage distribution of a) Ni b) V and c) Zn between 1) exchangeable, 2) bound to carbonates, 3) bound to Fe-Mn oxides, 4) bound to organic matter and sulfides, and 5) a residual fraction. Samples: bark ash and peat/coal co-combustion ash.

5.6.2 Optimization of sonication time in step iii

The recoveries for each analyte at each step were calculated by dividing the mean concentration of the element by the total leachable concentration (sum of all the steps) of the element. In some steps, for example in step iii the recoveries exceeded 100 %. This can be contributed to small number of replicate samples ($n = 2$).

Step iii (extraction of oxide fraction) was performed by extracting the residue from step ii with 10 ml of $0.04 \text{ mol l}^{-1} \text{ NH}_2\text{OH}\cdot\text{HCl}$ (pH adjusted to 2 with HNO_3). The power of sonication was observed especially in this step as all elements were leached better than by conventional extraction (time 6 h) by a sonication time of 12 min which was set as the optimized extraction time for this step (Fig. 7).

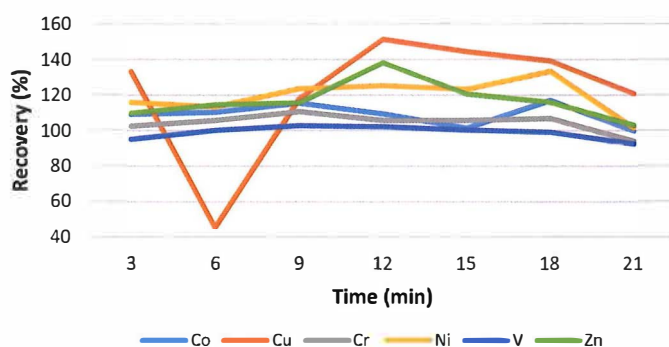


FIGURE 7 Optimization of sonication time in ultrasound-assisted sequential extraction in step iii of the ultrasound-assisted sequential extraction.

5.6.3 The element concentrations in oxide fraction

The extractability of Co, Cr, Cu, Ni, V and Zn in tandem with the matrix elements (Al, Ca, Fe, K, Mg, Mn, Na, P, Pb, S, Si, Ti, W) from three different fly ash samples (bark ash, sludge/peat ash, peat/coal ash) was studied using the ultrasound-assisted sequential extraction method.

Portions of Fe (4-26%) and Mn (27-64%) were naturally high in the oxide fraction. High portions of Ca (20-45%), Al (7-49%) and Mg (9-33%) were also detected from this fraction. This is probably attributed to the high content of CaO , Al_2O_3 and MgO in the ash samples.^{14, 36}

With the exception of peat/coal ash Mn (27-64%) was detected the most in this fraction. 48% of Co was leached bark ash. It can be seen that for all ashes investigated the second largest portion of elements Al (7-49%), Cu (9-24%), Co (7-48%), Fe (4-26%), Zn (11-38%) and V (24-42%) were observed from the oxide fraction. Additionally, notable portions of Ni (5-39 %) and Cr (4-16 %) were detected in this fraction. Lima *et al.*³⁸ estimated that 10% of Cr was in the

oxidation state of +6 in ash from the co-combustion of wood and oil. The oxides of Fe, Mn and Al adsorb Cr(VI) at a pH below 7 and at a low pH Cr(VI) is reduced to Cr(III) and liberated into solution.

5.6.4 Ultrasound-assisted extraction methods using ammoniumoxalate and oxalic acid

As discussed before, notable Al, Fe and Mn concentrations were detected from the oxide fraction of the sequential extraction. Additionally, notable portions of Co, Cr, Cu, Ni, V and Zn were liberated into the solution. However, the concentrations of Au, Ir, Pd and Pt were low in the leachates. As mentioned earlier, the elements Co, Cr, Cu, Ni, V and Zn can be regarded as sparsely soluble and are expected to show similar chemistry and thus similar leaching behavior to Au, Ir, Pd and Pt. The aims of the following study were divided into two:

- i) to optimize the ultrasound-assisted extraction method by which the noble metals could be recovered from fly ash samples. The method was optimized by observing the concentrations of Co, Cr, Cu, Ni, V and Zn.
- ii) to develop a method by which the noble metals can be recovered from the leachate resulting from step i (see chapters 5.6 and 5.7).

The leachability of oxides was evaluated by observing the leached Al, Fe and Mn concentrations. The recovery for each element was calculated by dividing the leached concentration by the concentration obtained from the total digestion. After initial tests it was observed that by using solutions of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and $\text{H}_2\text{C}_2\text{O}_4$ recoveries of Co, Cr, Cu, Ni, V and Zn from fly ash were higher than when solutions of $\text{NH}_2\text{OH}\cdot\text{HCl}$ ¹⁰⁸, $\text{CH}_4\text{N}_2\text{S}$ ^{137, 206-207}, HCl ^{8, 137}, HNO_3 ^{37, 8, 137} and H_2SO_4 ^{137, 207} were used. Thus they were selected for further tests. The parameters of ultrasound-assisted extraction were optimized using fly ash samples from the combustion of peat (70%) and wood residue (30%). The initial extraction tests were carried out in a centrifuge tube using a sample weight of 1 g and, later, optimized for the sample weight of 10 g (5.6.4.2).

Extraction tests using a sample weight of 1 g

The effects of L/S ratio, concentration of extraction solutions and sonication time on the leaching of precious metals were studied in individual tests. The maximum temperature used with the equipment, of 85 °C, resulted in the highest recoveries for the elements investigated. Tessier *et al.*¹⁴¹ suggested a temperature of 96 ± 3 °C to extract the Fe and Mn oxide fraction in their classical extraction scheme.

L/S ratio

From the results it was observed that a volume of 20 ml of extraction solution for a sample of about 1 g resulted in the highest recoveries of the elements investigated. Thus L/S of 20 ml g⁻¹ was the optimized L/S-ratio.

The concentration of extracting agent

The highest recoveries of Co, Cr, Cu, Ni, V and Zn were obtained by using 0.75 mol l⁻¹ oxalate solutions. The lower recoveries obtained by 1 mol l⁻¹ oxalate are probably attributed to co-precipitation of the elements into the oxalate precipitate formed. All in all, oxalic acid with no adjustment of pH was preferred to ammonium oxalate and selected as the extracting agent for further tests.

Ca might buffer the oxalate-rich solution and thus lower the extraction power of the extracting agent. Additionally, notable removal of Ca, Na and K by washing the fly ash has been reported in other works.^{29, 163, 208}

Thus, the usefulness of the washing step was investigated in this work. The fly ash was extracted in two steps as follows:

- i) 20 ml of 0.2 mol l⁻¹ HNO₃ at 40 °C for 9 min
- ii) 20 ml of 0.75 mol l⁻¹ H₂C₂O₄ at 85 °C for 18 min

The washing step was discarded as only a very small portion of Ca was removed in the first step. Additionally, the concentrations of Co, Cr, Cu, Ni, V and Zn were not notably enriched.

Sonication time

Statistically, no significant differences were found between the extraction with a sonication of 18 min and 78 min without ultrasound. Additionally, it was observed that when samples were left to stand in the water bath for 30 min between the ultrasound cycles the recoveries of Co, Cr, Cu, Ni, V and Zn improved slightly.

Thus, the optimized parameters obtained in extraction using a sample weight of 1 g are: 0.75 mol l⁻¹ H₂C₂O₄, L/S 20 ml g⁻¹, sonication at 85 °C with a time of 18 min divided into two periods (6 min + 12 min). After the first sonication period the samples are left to stand in the water bath for 30 min. Later it was observed that during the storage of samples a precipitate was formed in the bottom of the sample bottles. The possibility of carrying out the extraction by using more dilute H₂C₂O₄ was studied in the following extraction tests using a sample weight of 10 g.

Extraction tests using a sample weight of 10 g

In order to extract a larger sample weight the following extraction tests with oxalic acid were carried out in 500 ml Erlenmayer flasks. In tests the liquid-to-solid ratio, concentration of oxalic acid, extraction time and temperature were

optimized in each individual optimization test so that optimized parameters obtained in earlier optimization tests were always used. Additionally, the effect of sonication and mixing of the sample were investigated. The equipment used in ultrasound-assisted extraction is presented in Figure 8 a while the equipment used in the extraction without ultrasound is presented in Figure 8 b.

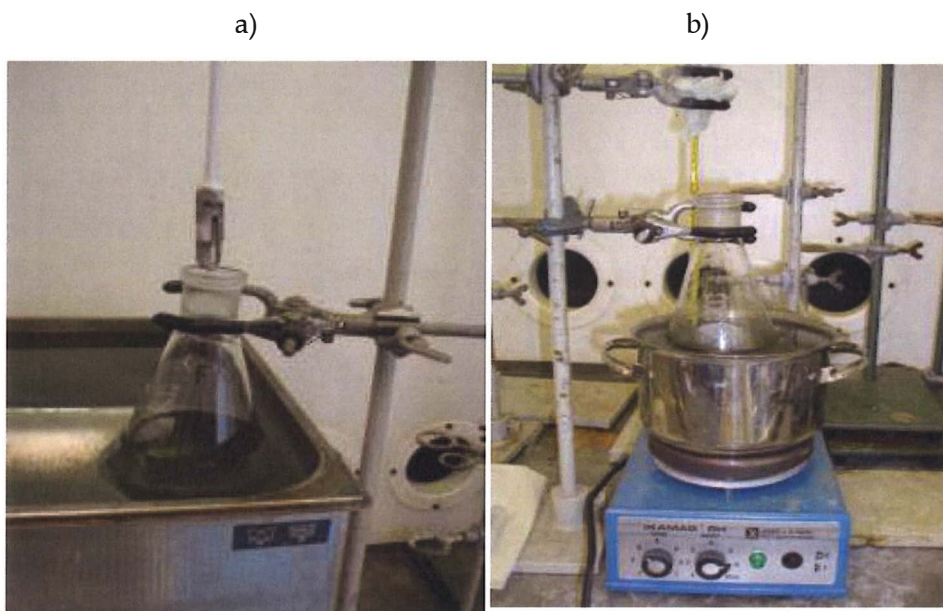


FIGURE 8 Equipment utilized in the extraction of the fly ash samples by ultrasound (a) and without ultrasound (b). Sample weight of 10 g. Both pieces of equipment allow continuous stirring during the extraction.

L/S-ratio

The L/S-ratio of 20 ml g⁻¹ optimized earlier was used throughout. The use of it produced comparable recoveries to the L/S-ratio 27 and the 40 ml g⁻¹ (paired t-test, p<0.05, Fig. 9). An L/S-ratio of 20 ml g⁻¹ was also recommended for the extraction of fly ash samples in the work by Kinoshita *et al.*²⁸

The power of ultrasound enabled the extraction of fly ash with a 10-fold higher sample weight with the same L/S-ratio which is a promising result when thinking about the possibility of using sonication in a larger scale extraction process.

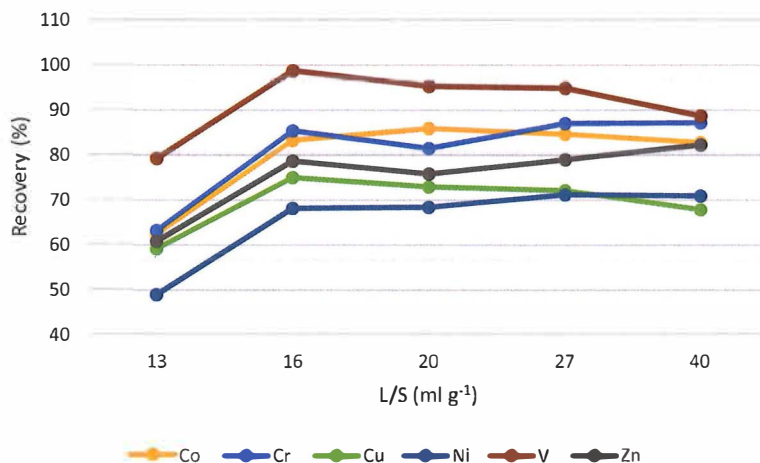


FIGURE 9 Effect of L/S-ratio on the extraction of selected metals. 0,75 mol l⁻¹ H₂C₂O₄, 75°C, sonication 6 min + standing 30 min + sonication 12 min.

Concentration of oxalic acid

The extraction using 0.45 mol l⁻¹ H₂C₂O₄ resulted in the highest recoveries of metals investigated. However, with 0.6 mol l⁻¹ of H₂C₂O₄ only slightly lower recoveries were obtained (Fig. 10). In the works of Wu and Ting¹⁶⁵ and Fedje *et al.*¹⁶¹ the use of 0.5 mol l⁻¹ of H₂C₂O₄ is suggested in the extraction of fly ashes. Compared to the results of Wu and Ting¹⁶⁵ higher recoveries of Fe, Mn and Zn while lower recoveries for Al and Cu were obtained in this work. Compared to the results of Fedje *et al.*¹⁶¹ higher recoveries for Al, Cu, Fe, Mn and Zn were obtained in this work. In some papers the method of using diluted H₂C₂O₄ with a high L/S-ratio^{163, 165} while in other papers the use of more concentrated reagent with low L/S-ratio is suggested.^{28, 29}

The use of the first method produces more waste solution to be treated than the latter method. Thus, from the point of view of an industrial metal recovery plant the latter option would be preferred. The consumption of oxalate is dependent on the concentration of metals in the solution. Because the elements of the composition of fly ash samples are different in the works a comparison of the results cannot be performed. It has been reported that Al, Mn and Zn were leached better with 0.1 mol l⁻¹ H₂C₂O₄ than by using 0.5 mol l⁻¹ H₂C₂O₄ from MSW fly ash samples.¹⁶⁵ and that the use of 0.1 mol l⁻¹ H₂C₂O₄ leached most Cr and Cu from sawdust, 81% and 62%, respectively.²⁰⁹

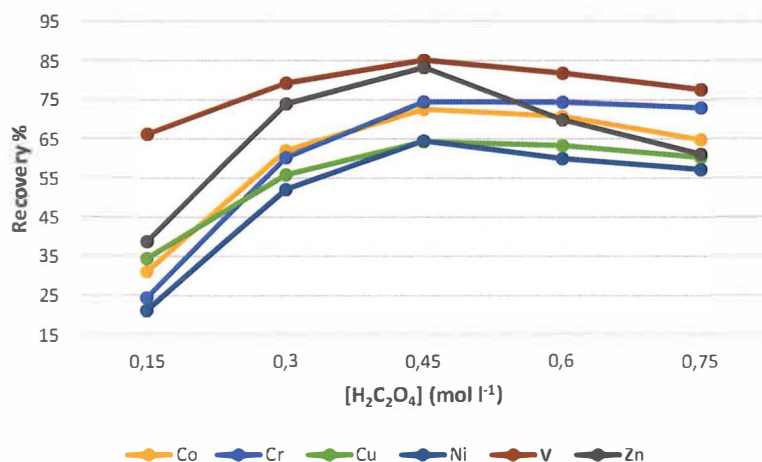


FIGURE 10 Effect of H₂C₂O₄ concentration on the extraction of selected metals. L./S 20 ml g⁻¹. 75 °C, ultrasound 6 min+standing 30 min+12 min.

It was observed that when the concentration of H₂C₂O₄ was higher than 0.6 mol l⁻¹ the precipitation of oxalate occurred. Thus, 0.5 mol l⁻¹ was selected as optimal concentration of the acid in the extraction. However, in the work of Kinoshita *et al.*²⁸, the concentration of oxalate used in extraction was twice that in the method recommended in this work. In that work and in the work of Zhang and Itoh²⁹, the extraction efficiency of 1 mol l⁻¹ H₂C₂O₄ was compared to three popular equimolar mineral acids (HNO₃, HCl and H₂SO₄) as an extracting agent. Kinoshita *et al.*²⁸ concluded that higher recoveries for Al and Fe but lower recoveries for Co, Cu, Mg, Mn and Zn from automobile tire waste fly ash were obtained than by using these equimolar mineral acids. Zhang and Itoh²⁹ concluded that by 1 mol l⁻¹ H₂C₂O₄ the recoveries of Na and Mg were highest and the ability of H₂C₂O₄ to extract Mn and Cr was second best after H₂SO₄. The recoveries of Al, Fe, Co, Cu, Ni, Ti, V and Zn were higher using mineral acids than by using H₂C₂O₄ in the extraction.

Temperature

The leachability of Co, Cr, Cu, Ni, V and Zn were highly dependent on temperature. The highest temperature studied, 75°C, resulted in the highest recoveries for all elements (Fig. 11). This is also the maximum temperature of the water bath in the ultrasound equipment when Erlenmeyer flasks are used. The effect of temperature in the extraction of Cu, Mn, Fe and Ti from tire waste fly ash samples by 1 mol l⁻¹ oxalic acid has been reported in one study.²⁸

When the temperature was raised from 23 °C to 60 °C 5 times more Cu, 4 times more Mn while 2 times more Fe and Ti were extracted. In this study, the increase in temperature from 25 °C to 65 °C increased the leaching of Cu, Fe and Mn by 86%, 131% and 62%, respectively.

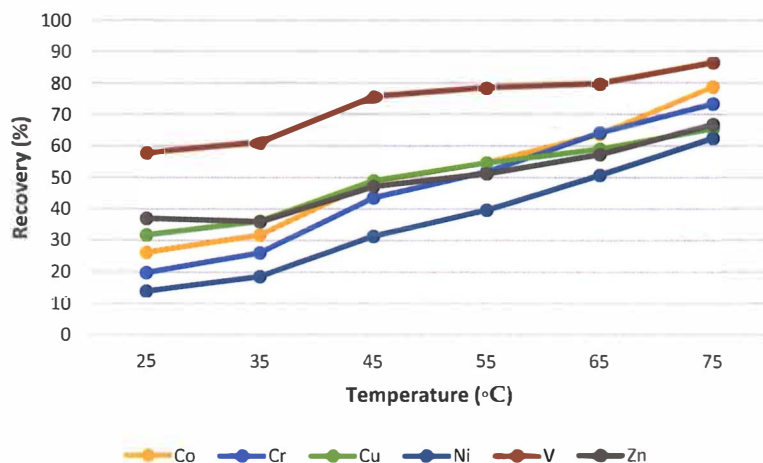


FIGURE 11 Effect of the temperature of water bath on the extraction of selected metals. L/S: 20 ml g⁻¹, 0.75 mol l⁻¹ H₂C₂O₄, sonication 6 min + standing 30 min + sonication 12 min.

Sonication time

The longest sonication time tested (12-120 min, Fig. 12) consisted of these steps: sonication 3+3 min + standing 30 min + sonication 3+3+3+3 min + standing 30 min + sonication 3+3+3+3 min, which resulted in the highest recoveries of Al, Fe, Mn, Co, Cr, Cu, Ni, V and Zn. The time is shorter than the reported time for ultrasound-assisted extraction¹⁶⁷ and conventional extraction^{27, 28, 160, 164, 167} by H₂C₂O₄ on fly ash samples. Additionally, the time is notably shorter than recommended in the extraction of the respective fraction (bound to Fe and Mn oxides) in conventional sequential extraction schemes.^{141, 142}

In addition to speeding up the extraction, the use of ultrasound resulted in more efficient leaching of oxide fraction than by the non-ultrasound extraction method which was tested with extraction times of 12-222 min. Presumably, after 120 min of sonication oxalate precipitate was formed and the elements investigated co-precipitated to some extent.

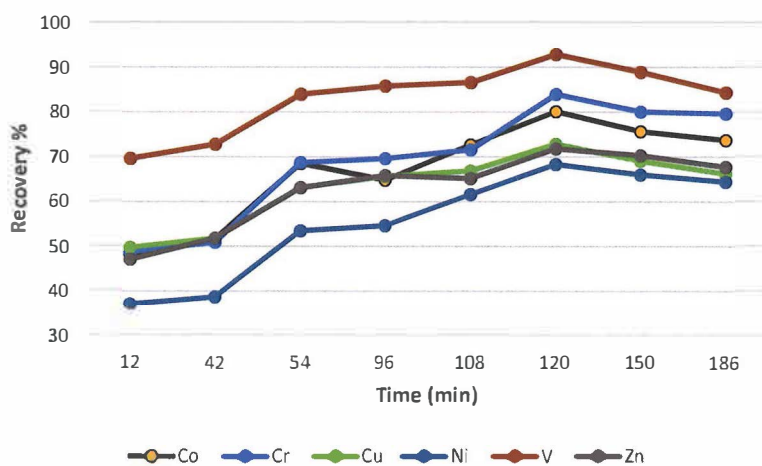


FIGURE 12 Effect of sonication time on the extraction of selected metals. L/S 20 ml g⁻¹, 0,75 mol l⁻¹ H₂C₂O₄, 75 °C.

The effect of sonication and stirring

Continuous stirring during the sonication was superior to occasional shaking (Fig 13). Only Zn was leached at higher recoveries without sonication. This was also observed earlier in the study by Stanišić *et al.*¹³¹ In the same study the conclusion was that by using ultrasound more Al, Cr, Cu, Fe, Na, K, Mn, Ni and Pb were leached from soil samples more than by continuous stirring.

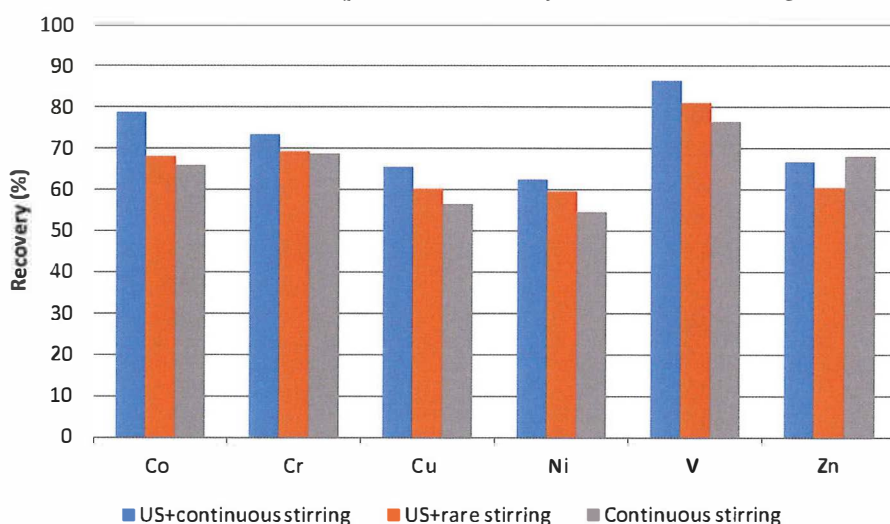


FIGURE 13 Effect of sonication and stirring. L/S 20 ml g⁻¹, 0,5 mol l⁻¹ H₂C₂O₄, 75 °C, sonication 120 min.

The optimized parameters in $\text{H}_2\text{C}_2\text{O}_4$ extraction by using a sample weight of 10 g are: 0.5 mol l^{-1} $\text{H}_2\text{C}_2\text{O}_4$, L/S: 20 ml g^{-1} , and a sonication time of 120 min at 75°C .

Statistical combination test of oxalic acid extraction

Tests where the individual effects of each variable of the extraction (L/S ratio, concentration of $\text{H}_2\text{C}_2\text{O}_4$, sonication time and temperature) on the leachability of elements Co, Cu, Cr, Ni, V and Zn from fly ash samples were studied statistically. A test sample matrix was planned and the test was performed by extracting the samples with random order. In the tests the sample weight of 1 g was used. Each variable was tested in two, estimated maximum and minimum, levels keeping the other variables constant. Thus, $2^4 = 16$ samples were extracted. For each variable, two levels ($6.25/25 \text{ ml g}^{-1}$, $0.35/0.85 \text{ mol l}^{-1}$, $25/75^\circ\text{C}$, $60/120 \text{ min}$) were utilised. Additionally, four replicate samples were treated using estimated average values (10 ml g^{-1} , 0.6 mol l^{-1} , 50°C , 90 min) of each variable (Table 23).

TABLE 23 Matrix of test samples.

| Test sample | $[\text{H}_2\text{C}_2\text{O}_4]$ (mol l^{-1}) | t (min) | T ($^\circ\text{C}$) | L/S (ml g^{-1}) |
|-------------|--|---------|------------------------|----------------------------|
| 1 | 0.35 | 60 | 75 | 25 |
| 2 | 0.85 | 60 | 75 | 25 |
| 3 | 0.35 | 60 | 75 | 6.25 |
| 4 | 0.85 | 60 | 75 | 6.25 |
| 5 | 0.35 | 120 | 75 | 25 |
| 6 | 0.85 | 120 | 75 | 25 |
| 7 | 0.35 | 120 | 75 | 6.25 |
| 8 | 0.85 | 120 | 75 | 6.25 |
| 9 | 0.35 | 60 | 25 | 25 |
| 10 | 0.85 | 60 | 25 | 25 |
| 11 | 0.35 | 60 | 25 | 6.25 |
| 12 | 0.85 | 60 | 25 | 6.25 |
| 13 | 0.35 | 120 | 25 | 25 |
| 14 | 0.85 | 120 | 25 | 25 |
| 15 | 0.35 | 120 | 25 | 6.25 |
| 16 | 0.85 | 120 | 25 | 6.25 |
| 17 | 0.6 | 90 | 50 | 10 |
| 18 | 0.6 | 90 | 50 | 10 |
| 19 | 0.6 | 90 | 50 | 10 |
| 20 | 0.6 | 90 | 50 | 10 |

The extraction using the L/S ratio of 25 ml g^{-1} and a temperature of 75°C resulted in the highest leached concentrations of Co, Cr, Cu, Ni and Zn (Fig. 14). By using average values for each variable in the extraction notably low recoveries were obtained. The values of the parameters for the four best test points with the

highest recoveries for Co, Cr, Cu, Ni, V and Zn are presented in Figure 14. With the exception of V, the highest recoveries were obtained using the values of the parameters as in test point 6, in which $0.85 \text{ mol l}^{-1} \text{ H}_2\text{C}_2\text{O}_4$ and a sonication time of 120 min were utilised. However, the results of test point 2 and test point 5 were not statistically significantly lower. This was observed as a result of a paired t-test (pairwise comparisons: test point 2 vs. test point 6 and test point 5 vs. test point 6). Thus, it can be concluded that if extraction is carried out using $\text{H}_2\text{C}_2\text{O}_4$ at a concentration of 0.35 mol l^{-1} , a sonication time of 120 min is required. On the other hand, extraction using $0.85 \text{ mol l}^{-1} \text{ H}_2\text{C}_2\text{O}_4$ requires an extraction of 60 minutes to produce equal results.

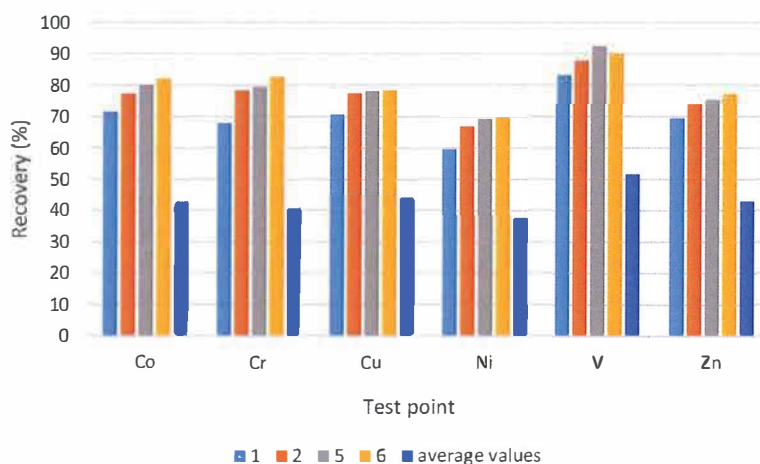


FIGURE 14 Combination test of $\text{H}_2\text{C}_2\text{O}_4$ extraction.

Effect of pre-wash with acidic water

The alkalinity of ash and leaching of impurities (Al, Ca, K, Na, S) were found to be detrimental for the recycling of the extracting reagent. Thus, whether the pH of the ash could be lowered was studied, and whether these elements could be removed by washing the fly ash with acidic water. In tests the effect of the pH of water, extraction time and liquid-to-solid ratio was studied. At the pH range of 4-5.5 no difference in leachability of the aforementioned elements was noted. The extraction of 60 min using an L/S-ratio of 25 ml g^{-1} leached the highest concentration of elements but, however, less than 1% of Ca, K and S and 2% of Al implied this was not a useful method for the fly ashes studied. However, the washing by acidic water can be useful for ash with a different composition as the removal of Na, K and Ca by 87% 76% and 48% of Ca from MSW fly ash has been reported in other works.^{29,163}

Recycling tests of oxalic acid

There is a possibility of recycling the leaching reagent after leaching is evaluated. Ideally, the leachate separated from the ash residue could be used in the leaching of the next fresh fly ash sample. Using this kind of methodology, a 10-staged leaching test using $0.5 \text{ mol l}^{-1} \text{ H}_2\text{C}_2\text{O}_4$ and L/S-ratio of 13.3 ml g^{-1} was carried out. The leachate solution after stage 1 was used to extract a fresh fly ash sample in step ii. Finally, the leachate solution after stage 9 was used to extract a fresh fly ash sample in stage 10. From previous tests it was observed that in each stage approximately 4% of liquid was lost as the ash particles captured the water molecules in their structure. To maintain the initial L/S-ratio (13.3 ml g^{-1}) at every stage of extraction the mass of fresh fly ash samples was always 4% lower than in the previous extraction stage.

During the test more $\text{H}_2\text{C}_2\text{O}_4$ was lost than expected. After the fourth, seventh and tenth stages the volume of $\text{H}_2\text{C}_2\text{O}_4$ recovered was 93, 77 and 43 % of the original volume, respectively. The concentration of valuable elements in recycled $\text{H}_2\text{C}_2\text{O}_4$ leachates didn't increase as expected. The pH of the liquids separated after leaching steps i and ii were 0.9 and 1.4, respectively. After stage 3 the pH had already increased to 3.4. This implies that by using the same $\text{H}_2\text{C}_2\text{O}_4$ solution only two fly ash samples can be leached because the leaching reagent is neutralized due to strongly alkaline ash. After four leaching stages a white precipitate, which presumably is CaC_2O_4 , was observed from the bottom of the centrifuge tubes.

5.7 Sulfide precipitation

5.7.1 Initial precipitation experiments

Next, a method by which the noble metals (Au, Ir, Pd, Pt) and Co, Cr, Cu, Ni, V and Zn could be recovered from oxalic acid leachate was studied. First, the possibility of recovering them by precipitation as sulfides was studied. The optimization test of the precipitation procedure was performed by using oxalic acid solution which resulted from the optimized extraction procedure as samples. In the sulfide precipitation optimization tests no standard addition was performed. The sulfide precipitation tests were carried out in 50 ml centrifuge tubes using $(\text{NI I}_4)_2\text{C}_2\text{O}_4$ or $\text{I I}_2\text{C}_2\text{O}_4$ leachates with a sample volume of 20 ml. It is worth mentioning that in other works where sulfide precipitation of metals has been investigated the equipment used has been different than in our experiments. For example Gharabaghi *et al.* used a glass reactor fitted with a reflux condenser in order to prevent liquid loss by evaporation when the sample is heated.¹⁸⁴

The parameters of precipitation (pH, precipitating agent, concentration of sulfide added, stirring and time) were studied in each individual test. The noble element concentrations were determined from dissolved precipitate samples by

ICP-OES. The precipitates were dissolved in 2 ml of *aqua regia*, transferred into a 10 ml volumetric flask and filled to the mark with water. The determined concentrations were corrected by using the MLR method validated earlier in the work (5.4.2).

5.7.2 Effect of precipitation agent

Based on literature, aqueous solutions of sodium sulfide (Na_2S), sodium hydrogensulfide (NaHS), and thioacetamide ($\text{C}_2\text{H}_5\text{NS}$) were used as precipitating agents in the experiments. Additionally, a mixture containing Na_2S (NH_4) $_2\text{SO}_4$ and NH_4Cl with different concentrations was tested in precipitation. Chloride was added to the sample solution as NH_4Cl since the precipitation of Ir as $(\text{NH}_4)_2[\text{IrCl}_6]$ ^{43,138} has been reported earlier.

The precipitation was carried out at pH 1.5 by applying 1 ml of 0.6 mol l⁻¹ solutions of Na_2S , $\text{Na}_2\text{S} + (\text{NH}_4)_2\text{SO}_4$, NaHS and $\text{C}_2\text{H}_5\text{NS}$ per 20 ml of oxalic acid leachate. Over 90% of Cu precipitated by all precipitation agents and additionally, of the matrix elements 40% of Pb with the exception of NaHS . Ir was precipitated most when Na_2S was used as a precipitation agent. The recoveries of Pd and Pt were slightly higher when NH_4Cl was used together with Na_2S (1 ml of 0.6 mol l⁻¹ $\text{Na}_2\text{S} + 1$ ml of 2.5 mol l⁻¹ NH_4Cl /20 ml of the sample). This is probably explained by the precipitation of them as $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ and $(\text{NH}_4)_2[\text{PtCl}_6]$.³⁰

The initial pH of the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and $\text{H}_2\text{C}_2\text{O}_4$ leachates were approximately 3 and 0.9, respectively. When the pH of $\text{H}_2\text{C}_2\text{O}_4$ was adjusted by NH_3 and the pH of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ by HCl the highest recoveries for the elements were obtained throughout. Thus these reagents were applied in the adjustment of pH in the following experiments.

5.7.3 Effects of pH

The precipitation was studied at pH 0-10 by using Na_2S as a precipitating agent. The pH was adjusted by NH_3 . The precipitate was formed in pH areas of about 0-3 and 7-8. The mass of precipitate was determined by weighing the same centrifuge tube before (as empty) and after (with the dried precipitate) the precipitation. It was observed that the mass of sulfide precipitate was at its maximum at pH 1.5 and 8.5. The following test confirmed that the precipitation of Ir and Cu occurred optimizedly at pH 1.5 while that of Pd, Pt and Au at pH 8.5. Bax *et al.*¹²¹ reported that 26.4% and 39.4% of Pd and Au precipitated as sulfides at pH 9.5 from cyanide leachate, respectively. The recovery of Co, Cr, Ni, V and Zn increased as a function of pH. (Fig. 15). This is in the line with that reported in other works where the pHs for sulfide precipitation of Cu, Co, Ni and Zn have been suggested as follows: Cu (pH 1.5-2), Co (pH 3-4), Ni (pH 3-7.5), Zn (pH 4.5).^{184, 187, 193, 210}

Finally it was observed that the first precipitation should be performed at pH 1.5. After separation of the precipitate the second precipitate was formed optimizedly at pH 8.5.

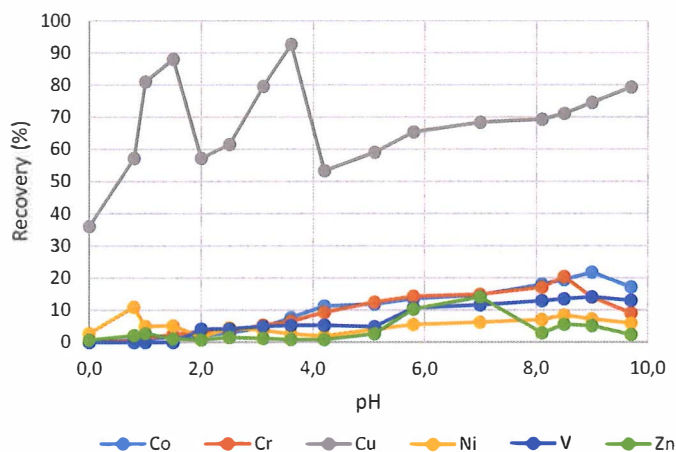


FIGURE 15 Recoveries (%) of Co, Cr, Cu, Ni, V and Zn in the sulfide precipitation as a function of pH. T = 25 °C.

5.7.4 Added concentration of sulfide

Since Cu, Ir and Pb were precipitated with the highest recoveries the added concentration of sulfide was optimized by observing the recoveries of these elements. By applying 1 ml of 0.6 mol l⁻¹ Na₂S per 20 ml of sample solution the highest recoveries Cu (91.4 %), Ir (93.5 %) and Pb (78.1 %) were obtained (Fig. 16). Karbanee *et al.*¹⁹⁸ performed batch aqueous and gaseous sulfide precipitation experiments in order to precipitate Ni by using Na₂S as a precipitating agent. They concluded that a sulfide waste problem was present when the NaOH : Na₂S (g) ratio was over 1.66 : 1. Then, either the accumulation of the reaction solution or there was no absorption of H₂S into the solution.

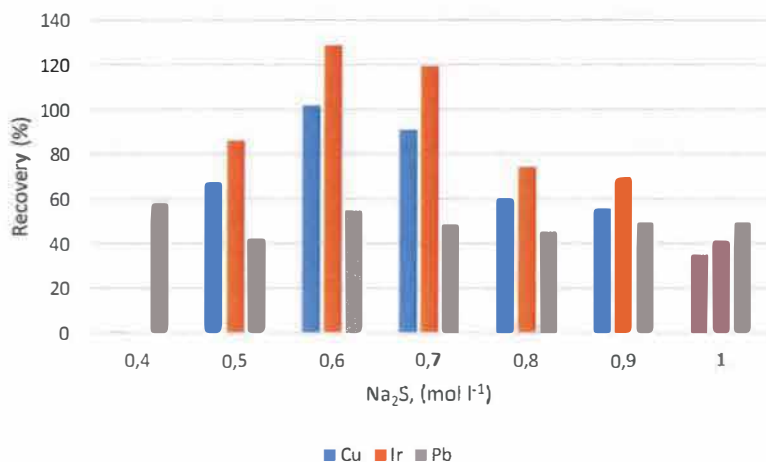


FIGURE 16 Effect of added concentration of sulfide. Sample: 20 ml of 0.75 mol l⁻¹ (NH₄)₂C₂O₄, precipitation reagent 1 ml of Na₂S solution, pH adjusted to 1.5 by HCl. Recovery of Ir, Cu and Pb (%).

5.7.5 Effect of temperature

The precipitation was performed in a water bath of which the temperature was varied between 30-87 °C. 1 ml of 0.6 mol l⁻¹ Na₂S + 1 ml of 2.5 mol l⁻¹ NH₄Cl was added into 20 ml of sample solution after which the pH was adjusted to 1.2 by 5 mol l⁻¹ NH₃. The samples were stirred continuously for 40 min after which the samples were left to cool.

Cu (90.1 %), Cr (2.7 %) and Pt (4.2 %) were precipitated the most when the highest temperature of the water bath was utilized. A temperature of 65 °C resulted in the highest precipitation of Ir (100 %), Au (2.7 %) and Ni (23.0 %) while at 30 °C Co (7.3 %) was precipitated the most. In the patent by Bax *et al.*¹⁹¹ the increase in temperature resulted in a higher precipitation of Pt and Au.¹²¹ A similar effect was not observed for Pd, Co, Cu and Ni. Gharabaghi *et al.*¹⁸⁴ reported that the precipitation of Cd, Cu, Ni and Zn was linearly dependent on the temperature at the range of 45-85 °C. Ni and Co were precipitated most specifically at 55 °C and at pH 4 from a chloridic solution in the work of Kaakkolammi.²¹⁰

5.7.6 Effect of contact time

It was observed that precipitation occurred immediately when the pH was adjusted to 1.5. However, prolonging the stirring time to 30 min increased the precipitation of Ir (100 %) and Cu (87.4 %). Thus, 30 min was set as an optimized time for precipitation. In the work of Gharabaghi *et al.*¹⁸⁴ the precipitation of CdS, CuS, NiS and ZnS was linearly dependent on the reaction time at the range of 5-45 min. This was attributed to the hydrolysis reaction of C₂H₅NS to H₂S and to more collisions between molecules at the optimized conditions.

5.7.7 Optimized sulfide precipitation procedure

To test the ability of the sulfide precipitation procedure to specifically precipitate the noble metals, a standard addition of Au, Ir, Pd and Pt (1 mg l^{-1}) was performed on samples before the precipitation. It was calculated that there was approximately 5 mol of sulfide per 1 mol of each noble metal. By using the optimized sulfide precipitation procedure presented in the experimental section (4.9), 100% of Pd, 96% of Au, 82% of Pt and 65% of Ir were precipitated at pH 1.5 (Figure 17). The rest of the Au was precipitated at pH 8.5. About 10% of Pt and nearly one third of Ir remained in the residue solution which separated from the precipitate at pH 8.5.

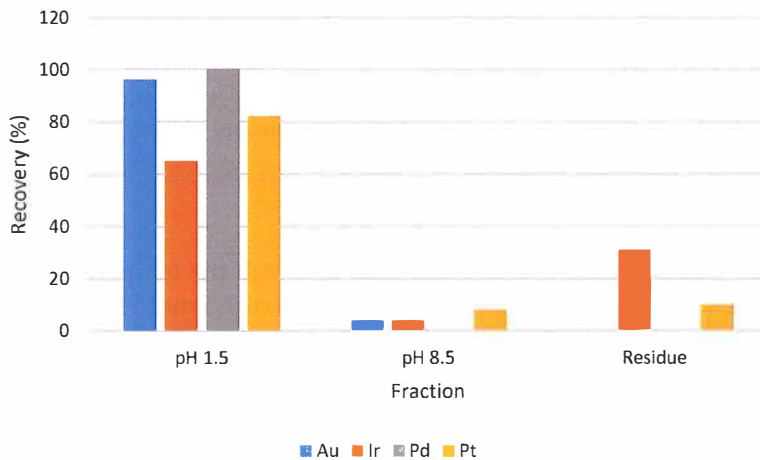


FIGURE 17 Percentual distribution of Au, Ir, Pd and Pt between three fractions using optimized sulfide precipitation procedure.

The enrichment factor (EF), determined as the concentration of the element in the precipitate divided by the concentration in the original ash was calculated for each element. As can be seen, Cu, Fe, Mn, Pb and Zn were more concentrated in the precipitate pH 1.5 while Al, P, Si and V were more concentrated in the precipitate pH 8.5 than in original fly ash (Table 24). The concentrations of Cr and Zn are notably lower in the precipitates than in the soil of Finnish mining areas while Cu was detected with a concentration detected from the mine area soils.

TABLE 24 Concentration of precious and matrix elements in sulfide precipitate samples (mg kg^{-1}) compared to respective concentrations in active Finnish mines. EF =enrichment factor.

| Element | Original fly ash leachate | Precipitate | EF | Precipitate | EF | Finnish active mines |
|---------|---------------------------|-------------|-------|-------------|-----|----------------------|
| | | pH 1.5 | | pH 8.5 | | |
| Cr | 93 | 50 | 0.5 | 20 | 0.2 | 88900 [211] |
| Cu | 280 | 2220 | 7.9 | 95 | 0.3 | 1300-11000 [212-214] |
| V | 65 | 21 | 0.3 | 220 | 3.4 | |
| Zn | 250 | 890 | 3.3 | 43 | 0.2 | 5000-26000 [211-212] |
| Al | 52900 | 3180 | 0.1 | 29300 | 0.6 | |
| Ca | 191000 | 6780 | < 0.1 | 200 | 0.0 | |
| Fe | 27000 | 120000 | 4.4 | 54300 | 2.0 | |
| K | 11600 | 720 | 0.1 | 1390 | 0.1 | |
| Mn | 1700 | 2840 | 1.7 | 200 | 0.1 | |
| Mg | 19300 | 4200 | 0.2 | 1040 | 0.1 | |
| P | 4400 | 400 | 0.1 | 12300 | 2.8 | |
| Pb | 47 | 72 | 1.5 | 14 | 0.3 | |
| S | 3600 | 149000 | 41.4 | 3900 | 1.1 | |
| Si | 180300 | 10400 | 0.1 | 71400 | 0.4 | |
| Ti | 930 | 24 | <0.1 | 480 | 0.5 | |

Of the matrix elements S (48%) and Fe (39%) were found to be the main components of the precipitate pH 1.5. The portion of other matrix elements were less than 3%. The mass portions of Au, Ir, Pd and Pt are around 1% for each precious metal. In the precipitate pH 8.5 Si (41%), Fe (31%) and Al (17%) were assigned as the main components. The sum of mass portions of Au, Ir, Pd and Pt covered only 0.3% of the precipitate. In comparison, Au, Pd and Pt are mined commercially in Kevitsa, Finland where the proven concentration of the metals in mineral reserves are 0.11; 0.15 and 0.20 mg kg^{-1} , respectively.²¹⁴

The sulfide precipitation at pH 1.5 can be regarded as quantitative but not specific for noble metals. Other hydrometallurgical procedures e.g. solvent extraction or ion exchange may offer more specific separation for the elements investigated. Thus, the recovery of noble metals by liquid-liquid extraction was investigated in further experiments.

5.8 The recovery of valuable metals by solvent extraction

Another recovery method tested was a solvent extraction (3.7). As the solvent extraction consists of two steps:

- i) the transform of the analytes into the organic phase (extraction phase)

- ii) the transform of the analytes back into the aquatic phase (stripping phase),

a suitable extracting reagent, pH, temperature and A/O ratio were studied for both steps of the extraction. In the optimization tests for both steps a synthetic solution ($[\text{H}_2\text{C}_2\text{O}_4] = 0.5 \text{ mol l}^{-1}$, $[\text{Au, Ir, Pd, Pt}] = 10 \text{ mg l}^{-1}$, $[\text{Al, Fe}] = 2000 \text{ mg l}^{-1}$; $[\text{Si}] = 400 \text{ mg l}^{-1}$; $[\text{Ca, K, Na}] = 200 \text{ mg l}^{-1}$ was used as an aquatic phase (A). In the optimization of the stripping phase a solution from the optimized extraction phase (4.10) was used as a sample. The recoveries in step 1 were calculated by dividing the determined concentration of the analyte in the aquatic phase by the added concentration of the analyte in the aquatic phase. For the stripping step the recoveries were calculated by dividing the determined concentration of the analyte in the organic phase by the added concentration of the analyte in the organic phase. The concentration of the analyte in the organic phase was calculated after the determination of concentration of the analyte in the aquatic phase.

Effect of extracting reagent

The solvent extraction of noble metals from synthetic oxalic acid solution was studied by using the following reagents: tributylphosphate (TBP), methyl isobutyl ketone (MIBK), diethyl malonate (DEM), dibutyl ether (DBE), tri-n-octylamine, and Aliquat 336® (quaternary amine). The reagents were diluted with kerosene, TBP, MIBK and ethyl acetate in the tests before the extraction. The dilution of the reagents decreased the viscosity and the phases were separated better. By the extraction of MIBK with a chloride concentration of 6 mol l^{-1} 100 % of Au, 76.6 % of Pd and 31.0 % of Pt were recovered (Fig. 18). Unfortunately, 100 % of Pb, 99.8% of Fe, 95.1% of Pb and 94.7 of Ge were co-transferred.

100% of Pd (TBP, DEM, ALIQ) and Pt (TBP) were recovered by applying highly acidic extracting reagents (Fig. 18). However, the addition of HCl and HNO_3 during the recovery process of Au, Ir, Pd and Pt seems not to be feasible since the recycling of the reagents becomes more complicated. By using Aliquat 336® 100 % of Au and Pd, 66.3 % of Pt and 14.0 % of Ir were recovered without the addition of HCl and HNO_3 . With other reagents Ir was not transferred to the organic phase.

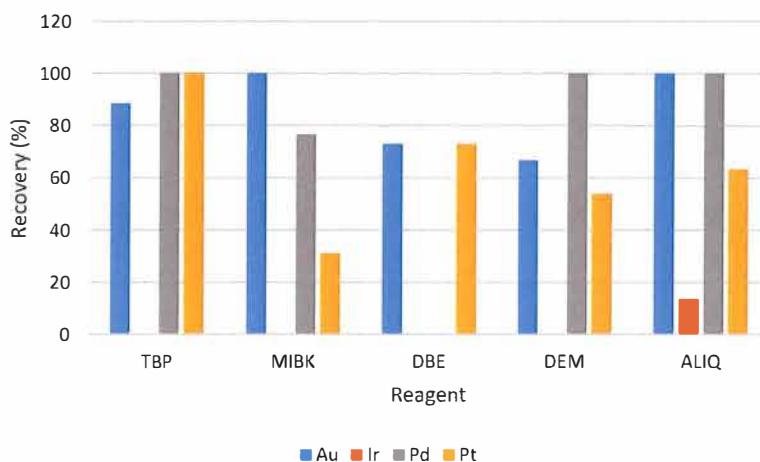


FIGURE 18 Highest recoveries obtained for Au, Pd and Pt by using the solvent extraction reagents: TBP (tributyl phosphate), MIBK (methyl iso butyl ketone), DBE (dibutyl ether), DEM (diethyl malonate) and ALIQ = Aliquat 336®.

| | TBP | MIBK | DBE | DEM | Aliquat 336® |
|---|-----|------|-----|-----|--------------|
| [HCl, mol l ⁻¹] | 5 | 5.7 | 0.9 | 3.2 | 0 |
| [HNO ₃ , mol l ⁻¹] | 2.4 | 1.3 | 0 | 1.3 | 0 |

When Aliquat 336® was diluted by MIBK and ethyl acetate two phases were formed while kerosene and TBP always formed three phases in the extraction. Ethyl acetate was preferred to MIBK as a diluent since less matrix elements were co-transferred to the organic phase.

Effect of stripping reagent

The following stripping reagents were tested: mixture of NaOH and NaCl, mixture of NH₃ + NH₄Cl and mixture of CH₄N₂S + HCl with varying concentrations. In the stripping phase the use of a solution which was 0.5 mol l⁻¹ with respect to CH₄N₂S and HCl resulted in the highest recoveries for Ir, Pd and Pt (about 70 %), which was reported earlier by Lee *et al.*¹⁷⁹ and Raju *et al.*¹⁷⁷ 80 % of Au was recovered with the highest recoveries by solution which was 0.25 mol l⁻¹ with respect to HCl and 0.5 mol l⁻¹ with respect to CH₄N₂S.

5.8.1 Effect of pH and temperature

The initial pH of the H₂C₂O₄ leachate was approximately 0.8 adjusted by NH₃. It was observed that Au was co-precipitated with calcium oxalate when the pH was raised. The solvent extraction tests were carried out at an ambient temperature and at 60 °C. In the latter case, calcium oxalate precipitate was formed in the

bottom of the separatory funnel. The further tests were thus carried out in an ambient temperature and without the adjustment of the pH of the $\text{H}_2\text{C}_2\text{O}_4$ leachate.

5.8.2 Effect of A/O ratio

The optimization tests for A/O ratios of extraction were performed as reported in the experimental section (4.8). The A/O ratio in the liquid-liquid extraction was optimized by using a synthetic solution ($[\text{H}_2\text{C}_2\text{O}_4] = 0.5 \text{ mol l}^{-1}$, $[\text{Au, Ir, Pd, Pt}] = 10 \text{ mg l}^{-1}$, $[\text{Al, Fe}] = 2000 \text{ mg l}^{-1}$; $[\text{Si}] = 400 \text{ mg l}^{-1}$; $[\text{Ca, K, Na}] = 200 \text{ mg l}^{-1}$, pH adjusted to 0.8 by NH_3) as an aquatic phase (A). The sample was combined with an organic phase (O) which was 4% tertiary amine, Aliquat 336 (v/v, in ethyl acetate), in an Erlenmeyer flask using different A/O ratios (10:1; 5:1; 2:1; 1:1; 1:2; 1:5). As the portion of the organic phase was increased higher recoveries for all noble metals, especially of Au and Pd were obtained. The highest recoveries for noble metals were obtained by using A/O of 1:5 (Table 25).

Before the optimization of the A/O ratio of back extraction, the organic phase was first loaded by performing the first part of the solvent extraction as above but using A/O of 1:1. Then the loaded organic phase (O) was extracted by the aquatic phase (A), which was 0.5 mol l^{-1} with respect to $\text{CH}_4\text{N}_2\text{S}$ and HCl, with A/O ratios 1:1, 1:4 and 1:8. 100% of Au, Ir and Pt and 78.3% of Pd were obtained by using A/O of 1:1 in the back extraction. Notably lower recoveries were obtained for Ir, Pd and Pt with A/O of 1:8. However, the enrichment factors of Au, Ir, Pd and Pt in the extraction with A/O of 1:8 were 6.1, 0.5, 1.7 and 4.2, respectively. Thus, concentrations of Au, Pd and Pt in the final solution were 6.1, 1.7 and 4.2 times higher than the respective concentrations in the original oxalic acid leachate. While the concentrations of Co, Cr, Cu, Ni, V and Zn were typically between $0.4 - 4.0 \text{ mg l}^{-1}$ in the oxalic acid leachates the respective concentrations in the samples resulting from back extraction with A/O of 1:8 were below 0.2 mg l^{-1} .

TABLE 25 Effect of A/O ratio. Noble elements recovered in liquid-liquid extraction and back extraction tests (%).

| Step of solvent extraction | A/O | Au | Ir | Pd | Pt |
|----------------------------|------|------|------|------|-------|
| Liquid-liquid extraction | 10:1 | 38.5 | 11.8 | 21.1 | 96.8 |
| | 5:1 | 60.7 | 13.1 | 23.9 | 90.8 |
| | 2:1 | 73.2 | 13.2 | 36.4 | 98.1 |
| | 1:1 | 78.5 | 13.3 | 45.7 | 100.0 |
| | 1:2 | 81.1 | 14.1 | 68.6 | 100.0 |
| | 1:5 | 81.1 | 14.0 | 89.6 | 100.0 |
| Back extraction | 1:1 | 100 | 100 | 78.3 | 100 |
| | 1:4 | 100 | 71.6 | 69.9 | 73 |
| | 1:8 | 97.3 | 47.7 | 45.7 | 52.8 |

5.8.3 Effect of extraction time

The optimization tests were performed as reported in the experimental section (4.8). In the liquid-liquid extraction the A/O ratio of 2:1 was used while in back extraction the A/O ratio of 1:2 was used. The times of 5, 10, 20 and 40 min were tested for both extraction steps. The liquid-liquid extraction of 5 min produced comparable results with a 40 min extraction time. Pd is probably precipitated from a solution when the extraction time is prolonged. In the test Au was precipitated completely when the extraction time of 10 min was used. In back extraction prolongation of the extraction time to 40 min increased the recovery of Pt. Thus, the time of 5 minutes for the first step and the time of 40 min for the second step of extraction were chosen.

All in all, the solvent extraction method was preferred to the sulfide precipitation method as much purer fractions of noble metals were obtained. The forming of metal complexes by tertiary amine Aliquat 336® (liquid-liquid extraction) and $\text{CH}_4\text{N}_2\text{S}$ - HCl solution (back extraction) with the noble metals occurred in the solution which enables the separation of them from basic metals. This has been reported in numerous works where the separation of them from chloridic media has been discussed. However, for the recovery of Co, Cr, Cu, Ni, V and Zn the extraction method is not recommended. Works by Fedje *et al.*¹⁷ and Schlumberger *et al.*²⁰ indicate that the recovery of Cu and Zn by liquid-liquid extraction from acidic media can be carried out with high recoveries. In order for the separation process of noble metals from fly ash leachates to be economically profitable the price of produced metals must exceed the production costs. Probably, as Karlsson *et al.*¹⁸ maintained, the circulation of the extracting agents—Aliquat 336®, ethyl acetate, $\text{CH}_4\text{N}_2\text{S}$ and HCl—is the crucial factor in the economic side of the separation process. Regeneration of the reagents also reduces the volume of waste generated in the process. Thus, further research on the circulation of the reagents is needed.

6 CONCLUSIONS

The hydrometallurgical recovery of selected valuable metals (Au, Co, Cu, Cr, Ir, Ni, Pd, Pt, V and Zn) from industrial bio fly ash samples was studied in this work. First, the concentrations of the elements (Au, Co, Cr, Cu, Ir, Ni, Pd, Pt, V, Zn) were determined from fly ash samples by ultrasound-assisted digestion followed by ICP-OES. Since the SRM sample applied did not contain the noble metals investigated in this work, the recovery test with the standard addition of noble metals at two levels of concentrations was performed. The determination of Au, Ir, Pd and Pt was found to be affected by spectral interferences due to the emission of the matrix elements Cu, Fe, Mn, Si, Ti and W. By the multiple linear regression method (MLR), the spectral interferences were eliminated totally for lines Pd 340.458 nm and Ir 224.268 nm while partly for lines Pt 214.423 nm and Au 267.595 nm. The leaching behavior of the valuable elements was evaluated by the ultrasound-assisted sequential extraction method. It was observed that notable portions of Co, Cr, Cu, Ni, V and Zn were liberated from the fly ash by specifically extracting the oxide fraction of the fly ash. Based on this observation, an extraction method was developed. The optimized ultrasound-assisted method with 120 min extraction time resulted in recoveries of 93, 84 and 80% for V, Cr and Co, respectively. The power of ultrasound accelerated the leaching of the metals significantly and this was also observed when the sample weight was increased to 10 g. This is a promising result when thinking about the possibility of using sonication in the larger scale extraction process.

The recovery of noble metals from oxalic acid leachate was studied in two widely used hydrometallurgical methods; solvent extraction and sulfide precipitation. The first recovery method studied, the sulfide precipitation method can be regarded as quantitative but not specific for the recovery of Au, Ir, Pd and Pt. 100% of Pd, 96% of Au, 82% of Pt and 65% of Ir were precipitated at pH 1.5. The rest of the Au was precipitated at pH 8.5. Around 10% of Pt and nearly one third of Ir remained in the residue solution and separated from the precipitate at pH 8.5. It was observed that the mass portions of Au, Ir, Pd and Pt in the precipitate at pH 1.5 were of about 1% for each precious metal. Of the precipitate at pH 8.5 the sum of the mass portions of Au, Ir, Pd and Pt covered

only 0.3%. The recovery of Co, Cr, Cu, Ni, V and Zn increased as a function of the pH, probably due to their more favourable precipitation as hydroxides.

The second recovery studied, solvent extraction, produced a higher degree of recovery for Au, Ir, Pd and Pt. Thus it can be preferred to the sulfide precipitation method. The strong anion exchanger of 4% tertiary ammonium salt solution, Aliquat 336®, transferred all the noble elements from H₂C₂O₄ leachate to the organic phase with the highest recoveries. The noble elements were back extracted optimizedly by a solution of 0.5 mol l⁻¹ with respect to CH₄N₂S and HCl. By using A/O of 1:5 in the first and 1:1 in the second extraction step the highest recoveries were obtained. However, when A/O-ratios of 1:1 and 1:8 were used in the respective extraction steps the concentrations of Au, Pd and Pt were improved 6.1, 1.7 and 4.2 times, respectively. The opposite was observed for Co, Cr, Cu, Ni, V and Zn implying that the liquid-liquid extraction method is not recommended for their recovery from oxalic acid leachate.

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