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Bc. Marek Straka

Examination of caesium concentration trends in extracts from cement blocks simulating radioactive waste

Výzkum trendů koncentrace cesia v extraktech z cementových bloků simulujících radioaktivní odpad

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Supervisor:

RNDr. Jakub Hraníček, Ph.D.

Consultant:

RNDr. Václav Červený, Ph.D.

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Declaration

I declare that I carried out this diploma thesis independently, and only with the cited sources, literature and other professional sources. I declare that this thesis has not been used to gain any other academic title.

In Prague on 13.1.2022

Marek Straka

Acknowledgement

I would like to thank all my family and friends for support.

Abstract

Cement is widely used as a solidification material of low and intermediate level radioactive waste containing caesium before shallow land burial. The aim of this thesis was to extract caesium out of 17 cement samples with 6 different cement binder compositions, by extraction with deionized water, then determine the amount of caesium in the extracts and look for trends in the extract Cs concentrations with various extraction duration. Cement samples, with stable caesium nuclide, were used to simulate retention of caesium in immobilized radioactive waste. Ten extractions from each sample in total were made with time ranging from 2 to 1032 hours. Atomic absorption spectrometry with flame atomization, using acetylene as fuel and air as oxidant, was used for caesium determination. This method was optimized and the addition of KCl serving as ionization buffer for better results was explored and compared.

Keywords

Atomic absorption spectrometry, flame atomization, caesium, extraction,

Abstrakt

Cement je nejčastěji využíván jako materiál pro ztužení nízko a středně radioaktivního odpadu obsahujícího cesium, před mělkým uskladněním v zemi. Cílem práce bylo extrahovat cesium ze 17 cementových vzorků s šesti různými složeními cementové směsi pomocí deionizované vody, následně stanovit množství cesia v extraktech a sledovat trendy ve změnách koncentrace cesia při různých délkách extrakce. Cementové vzorky obsahující stabilní nuklidy cesia byly použity k simulaci retence cesia v imobilizovaném radioaktivním odpadu. Celkem bylo provedeno 10 extrakcí z každého vzorku, s rozsahem délky extrakce od 2 do 1032 hodin. Pro stanovení cesia byla použita metoda atomové absorpční spektrometrie s plamenovou atomizací využívající acetylen jako palivo a vzduch jako oxidant. Tato metoda byla optimalizována, a zároveň byla prozkoumána a komparována možnost přidání ionizačního pufru ve formě KCl pro lepší výsledky.

Klíčová slova

Atomová absorpční spektrometrie, plamenová atomizace, cesium, extrakce

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List of abbreviations

AAS – atomic absorption spectrometry

CTU – Czech Technical University in Prague

F-AAS – atomic absorption spectrometry with flame atomization

HCL – hollow cathode lamp

LOD – limit of detection

LOQ – limit of quantification

MS – mass spectrometry

1. Goals and objectives

- Optimize method of determination by atomic absorption spectrometry
- Extract caesium from cement block samples
- Identify trends in caesium concentration values in extracts
- Compare results with and without addition of ionization buffer

2. Introduction

2.1. Alkali Metals

Alkali metals are a group of extremely reactive elements that belong to the first group of periodic table with ns^1 electron configuration, which explains their chemical and physical properties. In pure form they are very soft, have a characteristic silver metallic colour and a relatively low melting point. Due to their high reactivity they have to be preserved in an inert atmosphere, or submerged in kerosene. Alkali metals include lithium, sodium, potassium, rubidium and caesium. Sodium and potassium are abundant in the earth's crust but since they are present mainly in the form of compounds their recovery is an energy intensive process.^{2,3,4}

2.1.1. Caesium

Caesium with the lowest melting point among alkali metals is also the rarest, and only in recent history it began to be used commercially. It was discovered in 1860 in mineral water, by a newly developed method of flame spectrometry. In nature it is present as a monoisotope, and it can be found near the lake Bernic in Canada, in the form of a zeolite mineral, pollucite.⁵ The main source of caesium is, as a by-product of lithium processing. Commercial use for Cs is in photocells, as it easily releases electrons under the influence of light.⁵ It is also used in science in atomic clocks, where they use its transfer between basic and specific excited state and monitor the frequency of emitted electromagnetic radiation.^{2,3} Cs is a toxic pollutant and is not biodegradable, which makes monitoring of the Cs content in the environment very important.⁶ After the Chernobyl accident in 1986, radioactive caesium ^{137}Cs has hugely settled in in forests of Sweden. These radionuclides of Cs can be leached into the soil during rainfall, and are absorbed by wild fungi and game, often eaten by Swedish population, which is one of many cases for monitoring content of Cs in the environment.^{7,8}

2.1.2. Caesium determination

The easiest method of determination, is to let Cs react with hydrochloric acid and heat it on a Bunsen burner. It gives a specific blue colour flame. For quantitative analysis, the most common method is atomic absorption spectrometry, which also utilizes its characteristic atomic

spectrum.^{2,3} However, methods such as gamma-ray spectrometric determination, resonance ionization spectroscopy coupled with time-of-flight mass-selective ion detection, and a semiconductor diode laser spectrometer in a graphite-tube furnace.^{9,10,11} Gravimetric determination by precipitation by tetraphenylborate and radiochemical or epithermal neutron activation can also be used to determine caesium.¹² AAS measurements can be done either with flame, or electrothermal atomization.¹³ Electrothermal atomization is relatively repeatable and reasonably efficient.¹⁴ AAS coupled with flame atomization is often used for its sufficient accuracy with different types of samples, low sensitivity to interferences, speed and ease of operation, which are the reasons for choosing this method.^{13,15}

2.2. Atomic absorption spectrometry

Atomic absorption spectrometry (AAS) is a highly selective analytical method and one of the most simple, economical, and widely used techniques for element analysis.



Figure. 2.1. A photograph of GBC 933 AA atomic absorption spectrometer.

2.2.1. History

History of spectroscopy goes far into the 17th century when the first experiments with solar spectrum were performed. At the beginning of 19th century, the determination of exact position of spectrum lines was established. The explanation of origin of spectral lines came in 1859-1860 which opened the door for absorption and emission spectroscopy to be used for measurements in astronomy and chemistry.¹⁶

The first atomic absorption spectrometer was made in 1959 and was gradually developed to its current state. But its actual worldwide popularity was not immediate, due to the problems with low sensitivity caused by very narrow absorption lines. This problem was solved by using a special radiation source that radiates only a desired wavelength.¹⁶

2.2.2. Principle of atomic absorption spectrometry

It is based on the absorption of radiation, emitted by primary radiation source, by free atoms of the element which are usually in ground state. The determination is based on the Lambert-Beer law for absorption by free atoms of an element in gaseous state. The amount of radiation absorbed is relative to the concentration of the element and is the main principle for quantitative determination. Spectral range used with AAS is 190-900 nm and the selected wavelength for the analysis itself corresponds to the transition of the atoms between ground state and excited level. For the analysis itself only resonance transitions (transitions between ground state and excited state) are used.^{1,17,18}

2.2.3. Instrumentation of AAS

Typical atomic absorption spectrometer consists of primary radiation source, source of free atoms with sample introduction system, optical dispersive system, detector and electronics for data acquisition and processing.

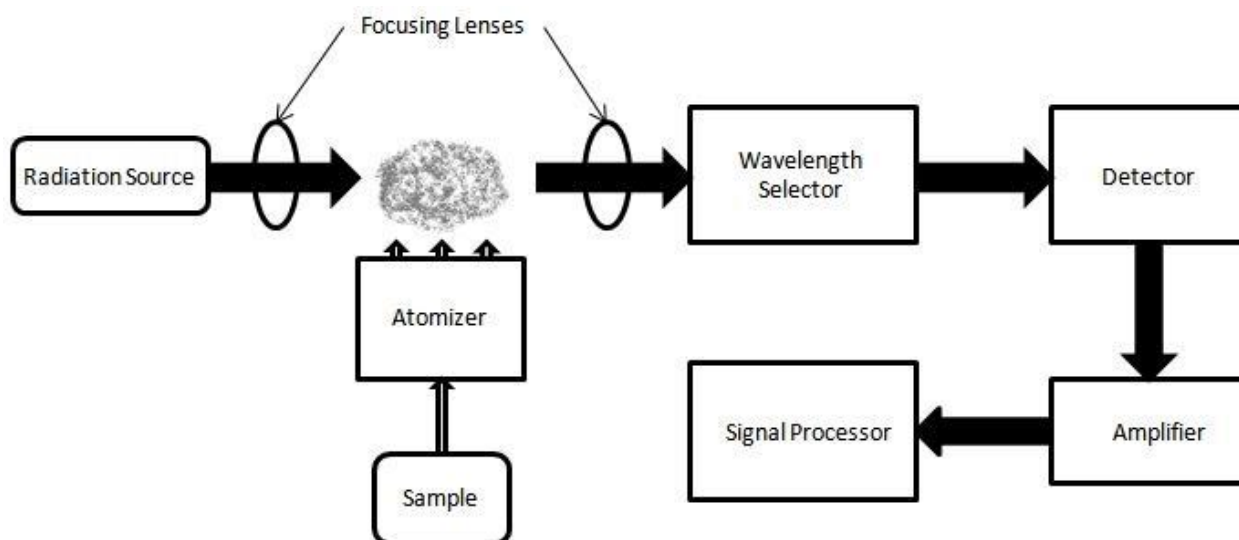


Figure 2.2. Diagram of atomic absorption spectrograph ¹⁹

2.2.3. Primary radiation source

The typical primary radiation source is usually a hollow cathode lamp (HCL) or electrodeless discharge lamp.¹ HCL consists of two electrodes encased in a glass tube filled with Ar or Ne gas at low pressure of about 100-200 Pa.¹⁷ At the end of the tube is a silica window transparent to UV-vis spectral range for light transmission. Voltage at the range of 200-600 V is applied on electrodes which leads to a current of 3-25 mA. Positive ions generated by the discharge are accelerated and crash into cathode releasing free atoms of the metal. The released atoms are excited by crashing into the positive gas ions or free electrons. Excited atoms returning to ground state radiate radiation specific to the used cathode material.

For anode a heat resistant metal like Zr, Ti, Ta, W or Ni is used to prolong its lifetime.^{1,17} The cathode is made out of highly pure metal or a mix of metals shaped into a hollow cylinder to cover the rest of the lamp from sputtered atoms of the metal, which happens during electrical discharge.¹

The main disadvantage of HCL is that it is element specific and can only measure the element which the cathode is made out of. This makes a multi-element analysis expensive and slow.²⁰ In the case of cathode being made out of several elements, more elements can be measured with one lamp, but at the cost of its lifetime since different elements have various volatilities.¹

To eliminate the need to change the radiation source for every new element to be determined a continuum source is used. Problem with using continuum source is that only a

small fraction of light is of the characteristic wavelength of the element. This would result in a low analytical sensitivity. To bypass this issue an Echelle grating monochromators with smaller spectral bandpass are used. It used to be the case, that the continuum radiation sources were not capable of reaching as high sensitivity as radiation sources with narrower linewidth. ¹ However, recent development in AAS technology has changed that.²¹ The most used continuum radiation sources are deuterium lamp and high intensity xenon arc lamp, which is preferred for its higher brilliance.¹

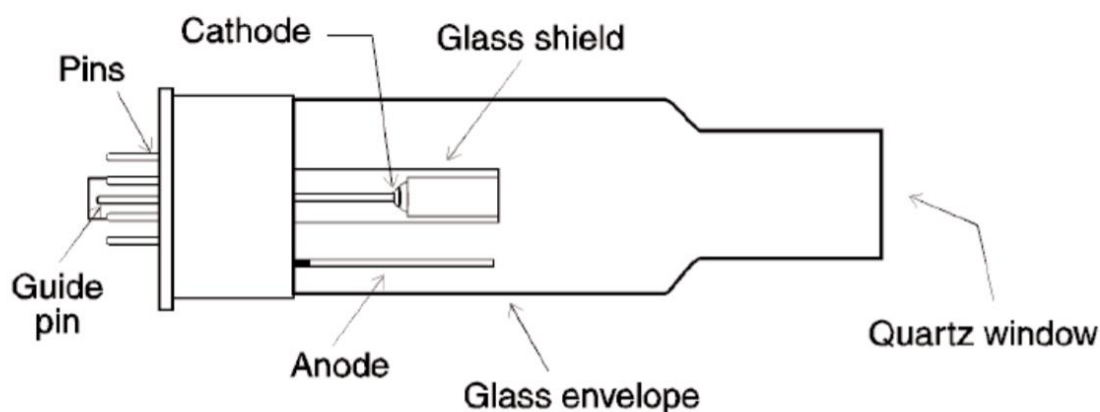


Figure 2.3. Diagram of a typical hollow cathode lamp.²²

2.2.4. Atomization

For the absorption of radiation by free atoms of the sample to be observed, the atoms of the sample need to be in an atomic and gaseous state.¹ The role of the atomizer is to efficiently convert the sample into free atoms mostly in ground state. Free atoms must be located in the light path between the radiation source and dispersive system.¹⁸ The most common methods for production of free atoms in gaseous state use thermal energy. For example flame atomization burns fuel and oxidizer, electrothermal atomization uses graphite tubes for sample introduction with electrical heating, and quartz tube atomizers use either electrical or flame heating. The efficiency of this transfer directly correlates to the sensitivity of the method.¹

Flame atomization uses acetylene as fuel and air or nitrous oxide as an oxidizer. Due to the high temperature of the flame, the sample is evaporated and thermal decomposition of the sample compounds to monoxides occurs. To ensure ideal mixture flow rate different sized slit

of titanium burner is used for different oxidizer and fuel mixtures, so the mixture flow speed is higher than the burning speed.¹⁷

2.2.5. Monochromator

The role of monochromator is to isolate different wavelengths so that only radiation of required wavelength will pass to the detector. Monochromators are usually equipped with a diffraction grating that separates these wavelengths. By rotating the grating, you can achieve passing of radiation of different wavelengths through the exit slit. Range of wavelengths that can pass through the monochromator is called spectral bandwidth, and is limited by exit slit width and dispersion of monochromator.²³ Placement of a monochromator between flame and photo-multiplier excludes most of the radiation created by chemiluminescent reactions in the flame.²⁴

2.2.6. Detector

Most of the atomic absorption spectrometers are equipped for measuring in UV-VIS spectral range. The detector uses photomultiplier, to turn radiation into signal, and is located after the exit slit. The detector then sends the signal into the computer, where changes in signal intensity are registered.²³

3. Experimental section

3.1. Reagents

Extraction of Cs was carried out in 1000mL polypropylene plastic reagent wide neck bottles. Deionized water ($< 0.07 \mu\text{S}$ ULTRAPUR) was used for extraction. Ionization buffer was prepared from 100 g.L^{-1} KCl solution (prepared from 99.5-100.5 % KCl, Sigma-Aldrich, Germany) by dilution in deionized water. Cs standards (prepared from Cesium Standard for AAS, $1000 \text{ mg.L}^{-1} \pm 4 \text{ mg.L}^{-1}$ Sigma-Aldrich, Germany) were prepared by dilution in deionized water.

3.2. Instrumentation

Cs determination was done on a GBC 933 AA (GBC Scientific Equipment Australia) atomic absorption spectrometer with flame atomization (acetylene-air). A Varian Techtron PTY hollow cathode lamp was used as a light source. Input parameters are listed in the table 3.1. Compressed acetylene was produced by Linde, Czech Republic and air was supplied by BAMAX Silent OLE compressor.

Table 3.1. Input parameters for GBC 933 AA.

Element	Cs
Wavelength [nm]	852.1
Supply current [mA]	15
Number of repetitions	3
Acetylene flow rate [mL.min^{-1}]	24
Air flow rate [mL.min^{-1}]	72

3.3. Samples

Cement is widely used as a solidification material of low and intermediate level radioactive waste containing Cs before shallow land burial.²⁵ Material for this use must have a suitable mechanical properties, permeability and high sorption capacity for radionuclides, which ensure its low leachability.^{26,27} However, the retention of Cs in cement matrix is negligible due to its

rather high water mobility and low chemical interaction with the cement.²⁸ The sorption of Cs in cement is low, and diffusivity of Cs in hydrated cement is high. A mix of cement with a material, with significant sorption capacity is a common practice in storage of radioactive waste.

Cement samples, that were used, simulate immobilized radioactive waste. Normally the Cs found in the cement are radioactive nuclides, and extractability of Cs is determined by change of radioactivity over time. But in this case a stable nuclide was present in the sample and extractability was determined using AAS.^{29,30}

The cement samples used, acquired from CTU, were made from a model evaporate concentrate without radionuclides based on a study by Szalo and Žatkuřák.³¹ It composed of NaOH (72.9 g.L⁻¹), KOH (14.9 g.L⁻¹), H₃BO₃ (76.0 g.L⁻¹), Na₂SO₄ (3.5 g.L⁻¹), NaNO₂ (14.5 g.L⁻¹), NaNO₃ (27.1 g.L⁻¹), NaCl (2.0 g.L⁻¹), C₆H₈O₇ (1.6 g.L⁻¹) and C₂H₂O₄.2H₂O (2.8 g.L⁻¹). These separate compounds were mixed with distilled water that was used as a mixing water with cement composites.

6 different cement composite mixes were used as binders, based on previous studies and experiments (see table 3.2.)^{32,33,34,35,36}. Water-binder ratio of 0.4 and 0.5 was used.

Table 3.2. Cement binder composition.

Abbreviation	Composition
SAC	100 % calcium-sulpho-aluminate cement
NP	50 % non-gypsum cement + 50 % Portland cement 42.5 R
NM	50 % non-gypsum cement + 50 % metakaolin
NP_M	50 % non-gypsum cement + 45 % Portland cement 42.5 R + 5 % metakaolin
NP_Z	50 % non-gypsum cement + 45 % Portland cement 42.5 R + 5 % natural zeolite
NM_Z	50 % non-gypsum cement + 45 % metakaolin + 5 % natural zeolite

To avoid volume changes a 40 wt% of pure fine silica aggregate, supplied by Sklopisek Střeleč, Czech Republic, was added.

In total 17 samples were obtained. The cement samples were of square prism shape with 2x2x10 cm dimensions. All samples were submerged in deionized water for 30 seconds and placed in a polypropylene plastic 1000mL bottle, with 880 mL of deionized water. After 2 hours, cement block was removed with plastic tweezers, left to drip and placed in another bottle for another extraction. This process took less than 5 seconds each time. The solution was stirred

and two 50 mL samples were taken from each bottle into 50 mL centrifuge test tubes. The remaining content was disposed of, and the bottle was rinsed with deionized water. A control measurement was done for impurities in the bottle. This procedure was repeated 10 times in total for each extract, with extraction time ranging from 2 to 1032 hours. For each sample a new fresh deionized water was used, that was controlled for Cs impurities before sample insertion. Duration of extractions is listed in table 3.3. When cement sample comes in contact with deionized water, the soluble compounds in the sample move into the surrounding water. This is caused by the dissolution, or chemical reaction, with chemical compounds in the deionized water.³⁷

Table 3.3. List of duration of extractions.

Number	Duration [h]
1	2
2	5
3	17
4	24
5	24
6	24
7	24
8	336
9	672
10	1032

4. Results and discussion

In total seventeen samples of cement blocks were used. Each sample was extracted 10 times. Extracts were then measured using atomic absorption spectrometry with flame atomization (F-AAS). Measurement method was optimized for beam height and acetylene flow rate. Addition of ionization buffer was tried and tested. LOD and LOQ were determined. The possibility of influence of water source was also investigated.

4.1. Optimization of AAS

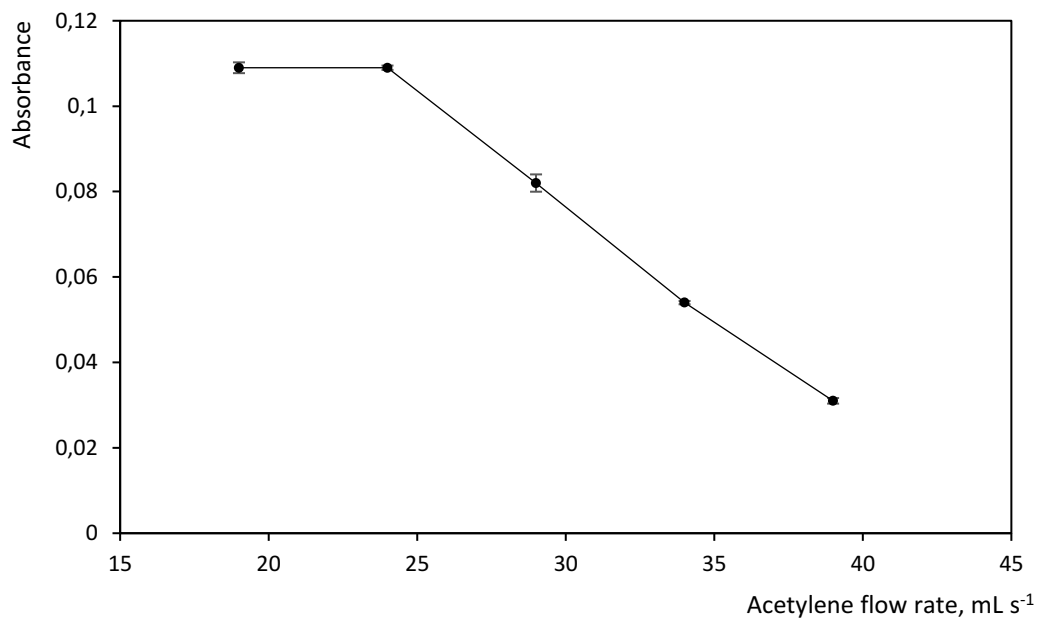
Beam height and acetylene flow rate were optimized for AAS spectrometer. Actual acetylene flow rate had to be experimentally measured, since the AAS spectrometer adjustment knob for acetylene flow rate, air flow rate and beam height is using relative units. This was done using acetylene intake hose introduced inside a reversed graduated cylinder submerged in water, filled with water and measuring the volume of expelled water per time. Values of acetylene flow rate obtained with this method are thus only indicative. Air flow rate could not be measured using this method since for the air to have restricted flow rate it needs resistance in the fog chamber. Air flow rate was calculated from data measured for acetylene flow rate, based on the presumption of AAS spectrometer using the same relative units for acetylene and air flow rate. Beam height was measured using a square ruler.

Five different acetylene flow rates were tested and we can see a steady decline of Cs signal with increasing acetylene flow rate (Figure 4.1.A). This is due to dilution of free Cs atoms in the optical path with higher volume of acetylene introduced. Optimal flow rate for acetylene was determined to be $24 \text{ mL}\cdot\text{s}^{-1}$.

The optimization of beam height was done for beam heights between 4 and 23 mm. In figure 4.1.B we can see gradual increase in absorbance with decreasing beam height. This is due to the optical path being closer to the space where atomization occurs and lower free Cs atoms dissipation. Optimal beam height was determined to be 4 mm.

The list of all optimized and calculated parameters is listed in table 4.1.

A)



B)

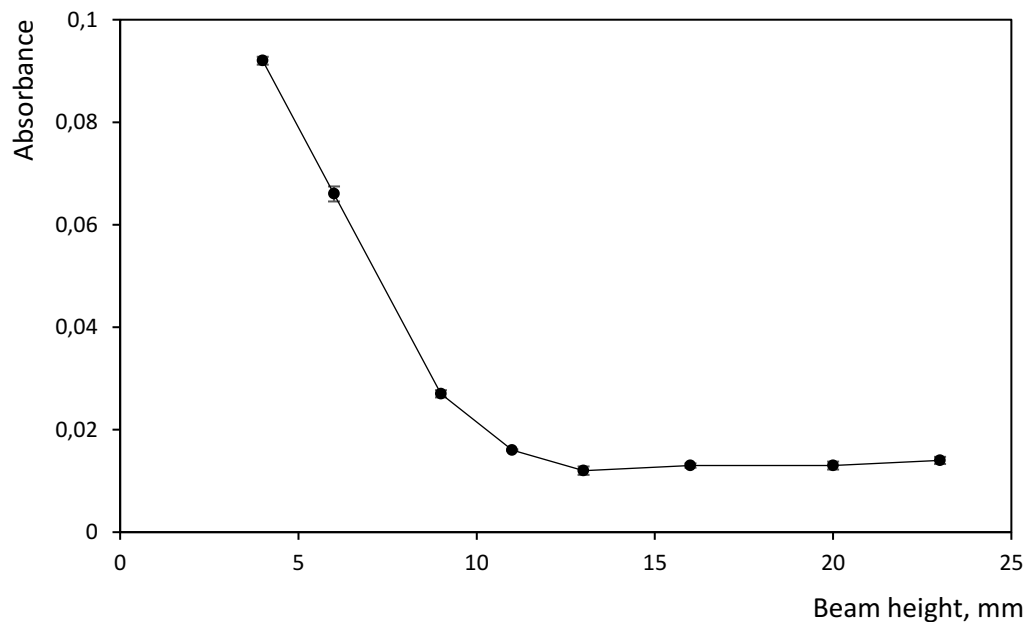


Figure 4.1. Effect of different acetylene flow rate (A) and beam height (B) on Cs signal intensity with F-AAS detection. Cs standard concentration 10 mg.L⁻¹. If not being a parameter to be optimized, beam height was 4 mm, air flow rate 72 mL.min⁻¹ and acetylene flow rate at 24 mL.min⁻¹. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

Table 4.1. Summary of optimal conditions and calculated limits of detection and quantification

Measured parameter	Optimal/calculated value
Beam height	4 mm
Acetylene flow rate	25 mL.s ⁻¹
Air flow rate	72 mL.s ⁻¹
LOD	0.116 mg.L ⁻¹
LOQ	0.386 mg.L ⁻¹

4.2. Addition of ionization buffer

Ionization can be the cause of non-linearity of calibration curve. This could generate the need for larger number of calibration solutions needed, or loss of sensitivity in the lower range of concentrations, or diversion from calibration curve in higher ranges of concentrations.^{38,39} The possibility of addition of ionization buffer was examined. Adding an excess of easily ionized element, such as Cs (ionization energy 3.9 eV) or K (ionization energy 4.34 eV),⁴⁰ acts as an ionization buffer by producing large excess of electrons in the flame.³⁸ This causes that the ionization buffer will be ionized instead of analyte, preventing a decrease in signal.⁴¹ Both CsCl and KCl were considered to be used as ionization suppressor but due to our analyte being Cs, KCl was chosen for its better suitability, availability and lower cost as the better option.⁴²

The possibility was experimentally tested with Cs standards with concentration of Cs ranging from 1 to 10 mg.L⁻¹. Addition of ionization buffer was determined to have positive effect on absorbance level (see Figure 4.2.). The increase in absorbance level can be attributed to the partial pressure of electrons produced by ionization buffer, which shifts ionization equilibrium of the analyte in favour of uncharged atoms. Thus, if the sample contains an element other than the analyte, that is easily ionized, it decreases the ionization of the analyte while increasing its signal.³⁸

However, addition of ionization buffer had no effect on trend line of extracts measurements (see Figure 4.2.), and was therefore not used for extracts.

The addition of KCl also had positive effect on linearity and accuracy. Still, the linearity of calibration curve without ionization buffer was acceptable, the determination coefficient was almost the same (0,9938 compared to 0,9978 with KCL).

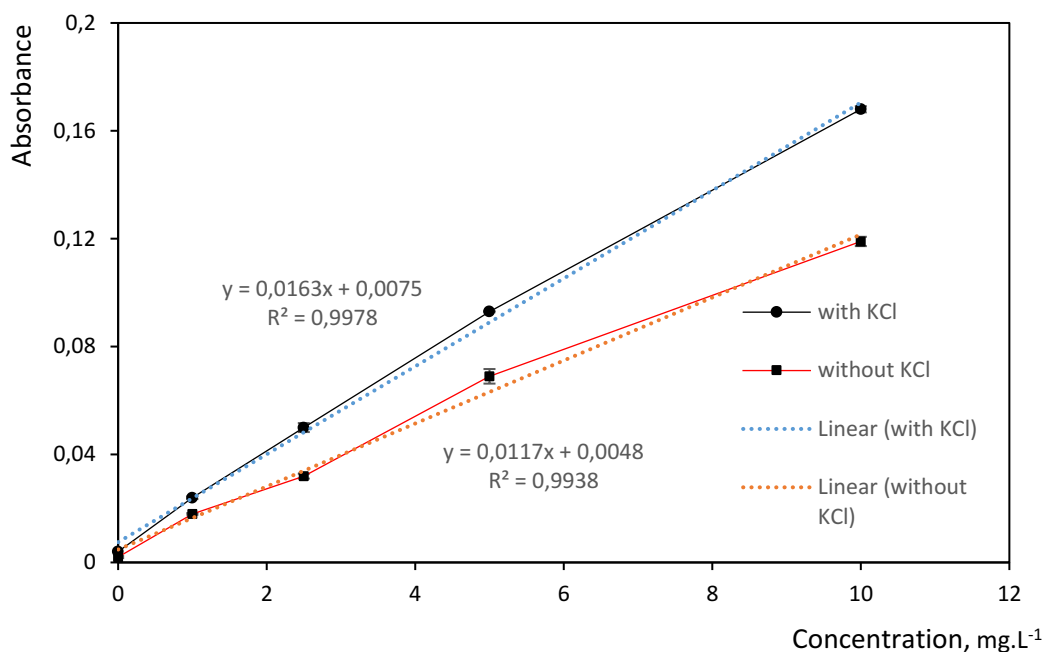


Figure 4.2. Effect of addition of KCl (ionization buffer) on Cs signal level. Cs standard concentration 10 mg.L⁻¹. Beam height was set to 4 mm, air flow rate 72 mL.min⁻¹, acetylene flow rate at 24 mL.min⁻¹. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

4.3. Limit of detection

Five measurements were made with Cs concentration of 10 mg.L⁻¹, each with 3 repetitions. LOD was calculated to be 0.116 mg.L⁻¹ and LOQ 0.386 mg.L⁻¹ (table 4.2.) as depicted below, character b being regression line directive.

Table 4.2. Results of standards measurements with calculated standard deviation, regression line directive, limit of detection and limit of quantification.

Sample number	Concentration of Cs [mg.L ⁻¹]
1	9.89
2	9.79
3	9.48
4	9.97
5	9.20
Average	9.47
Standard deviation	0.39
Regression line directive	10.13
LOD	0.116
LOQ	0.386

$$LOD = \frac{3 * SD}{b}$$

$$LOD = \frac{3 * 0.39}{10.13}$$

$$LOD = 0.116 \text{ mg/L}$$

$$LOQ = \frac{10 * SD}{b}$$

$$LOQ = 0.386 \text{ mg.L}^{-1}$$

4.4. Influence of water source

To be sure that there is no influence from source of water used for Cs extraction on the results of Cs concentration in extracts, three different sources of water were tested. There was no observable effect on signal intensity and no detectable amount of Cs impurities found (table 4.3.). Since there was no effect of water source on Cs detection accuracy, ULTRAPUR deionized water source was used, as it was most available for use.

Table 4.3. Effect of water source on Cs concentration in water.

* Conductivity according to the manufacturer

^x Values below LOD

Sample	Conductivity (μS)*	Concentration of Cs (mg L^{-1})	Average standard deviation
ULTRAPUR deionized water	0.07	0	0
Milli Q twice deionized water	0.055	0.001 ^x	0
ROWAPUR distilled water	18.33	0.002 ^x	0.0003

4.5. Results of measurement of extracts

Ten extracts in total were made out of each cement block sample and Cs concentration was measured in these extracts using F-AAS.

Extracts were separated into 6 groups based on their binder composition (table 3.2.). The measurements with addition of ionization were also separated into 6 groups based on their binder composition.

Calibration curve was measured (Figure 4.3.) with 7 Cs standard concentration levels, 1, 2.5, 5, 10, 25, 50 and 100 mg.L^{-1} under optimal conditions (see tables 3.1. and 4.1.).

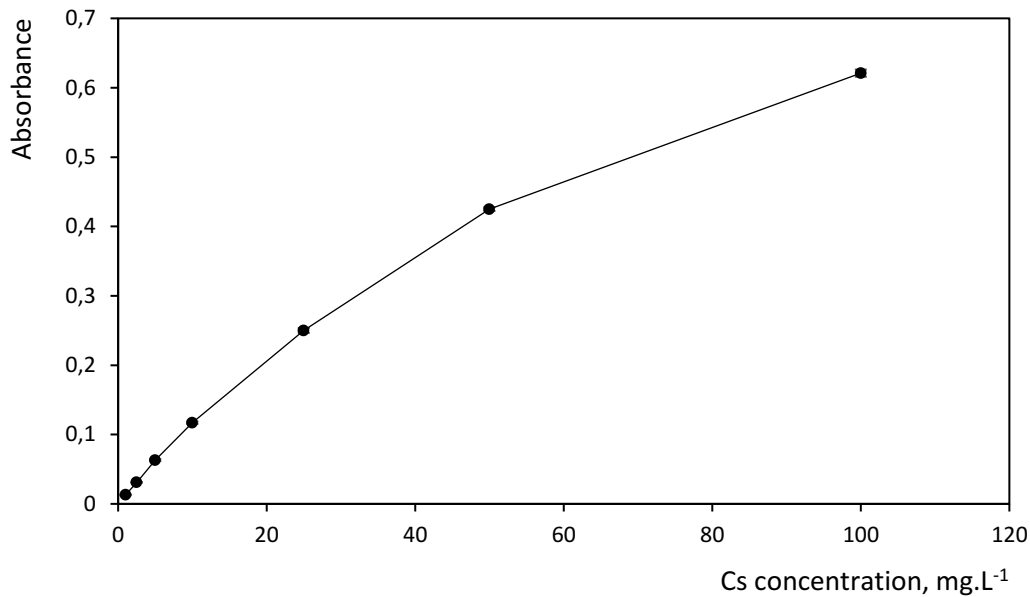


Figure 4.3. Calibration curve for Cs measured with F-AAS. Beam height was set to 4 mm, air flow rate 72 mL.min⁻¹, acetylene flow rate at 24 mL.min⁻¹. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

4.5.1. Results of extracts without ionization buffer

In figure 4.4. are depicted the results of group NP which cement binder composed of 50 % non-gypsum cement and 50 % Portland cement 42.5 R. From 2 to 5-hour extractions we could see a small decline in concentration, followed by a small rise to 17-hour extraction. The four 24-hour extractions showed a small decline with each consecutive extraction. This was probably due to depletion of Cs on the surface of the sample. At the 336-hour extraction a steep rise in Cs concentration was observed, which was probably caused by disruption or dissolution of ions on the outer layer of the concrete sample into the water, that were protecting the rest of the Cs in the sample. The 672-hour and 1032-hour extractions saw a stable decline in Cs concentration, probably due to depletion of Cs in the sample.

In groups NP-M (figure 4.5) we can see a difference at 336h extraction with extracts NP-M-0,5 2 and NP-M-0,5 3, which did not show a rise in concentration. This difference was probably due to lower porosity of the cement material, and differences during manufacturing process.

Groups NP-Z (figure 4.6.) and SAC (figure 4.9.) had very similar results as group NP-M with little diversity. Groups NM (figure 4.7.) and NM-Z (figure 4.8.) had comparable trends,

but about three times smaller Cs concentration. This was presumably due to lower Cs sorption capacity of the cement material.

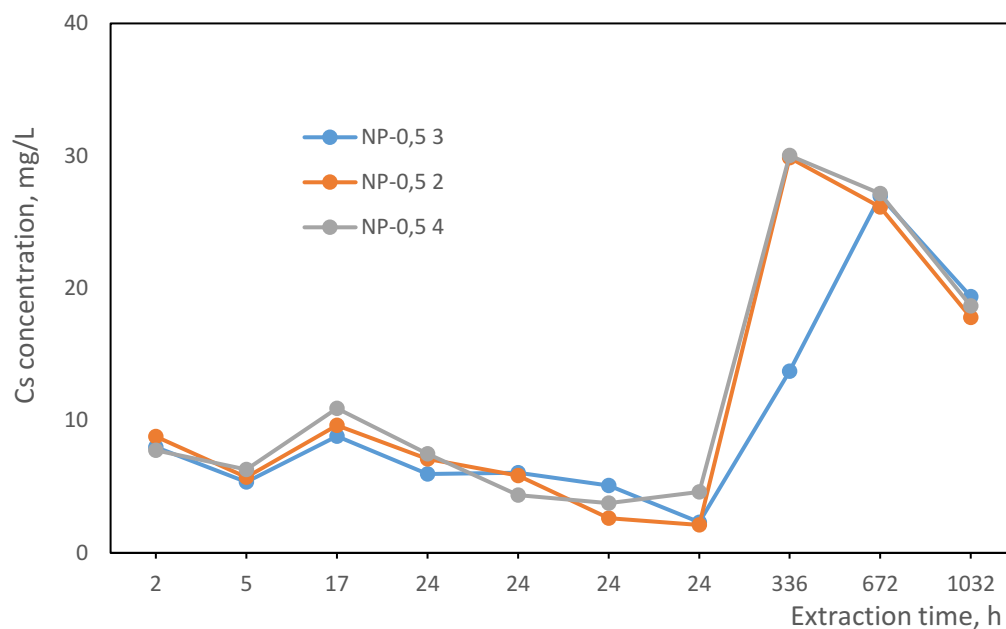


Figure 4.4. Concentration of Cs in group NP. Beam height was set to 4 mm, air flow rate 72 mL.min⁻¹, acetylene flow rate at 24 mL.min⁻¹. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

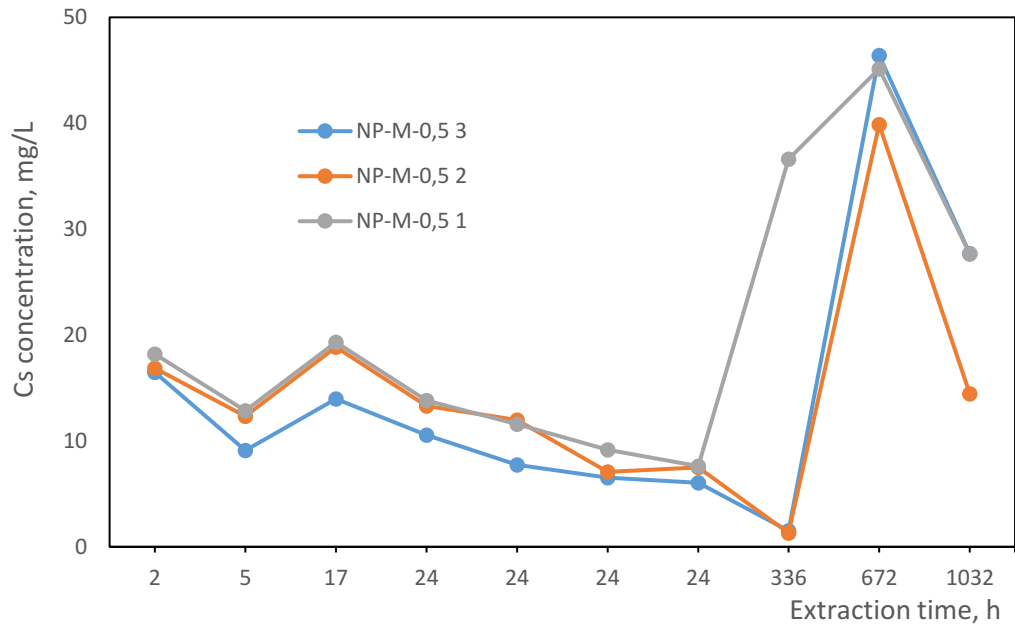


Figure 4.5. Concentration of Cs in group NP-M. Beam height was set to 4 mm, air flow rate 72 mL.min⁻¹, acetylene flow rate at 24 mL.min⁻¹. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

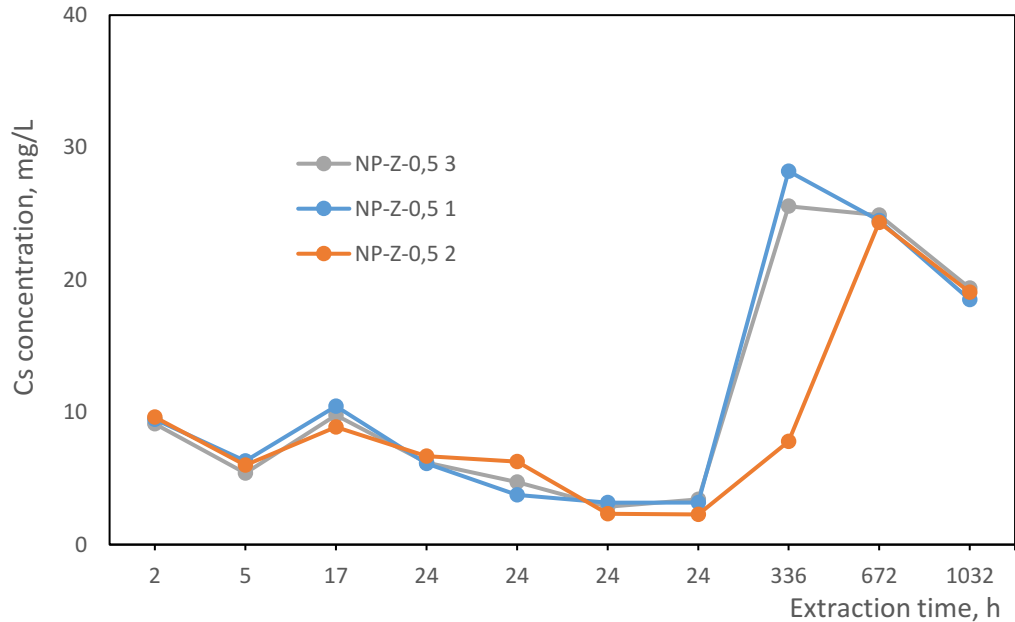


Figure 4.6. Concentration of Cs in group NP-Z. Beam height was set to 4 mm, air flow rate 72 mL.min⁻¹, acetylene flow rate at 24 mL.min⁻¹. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

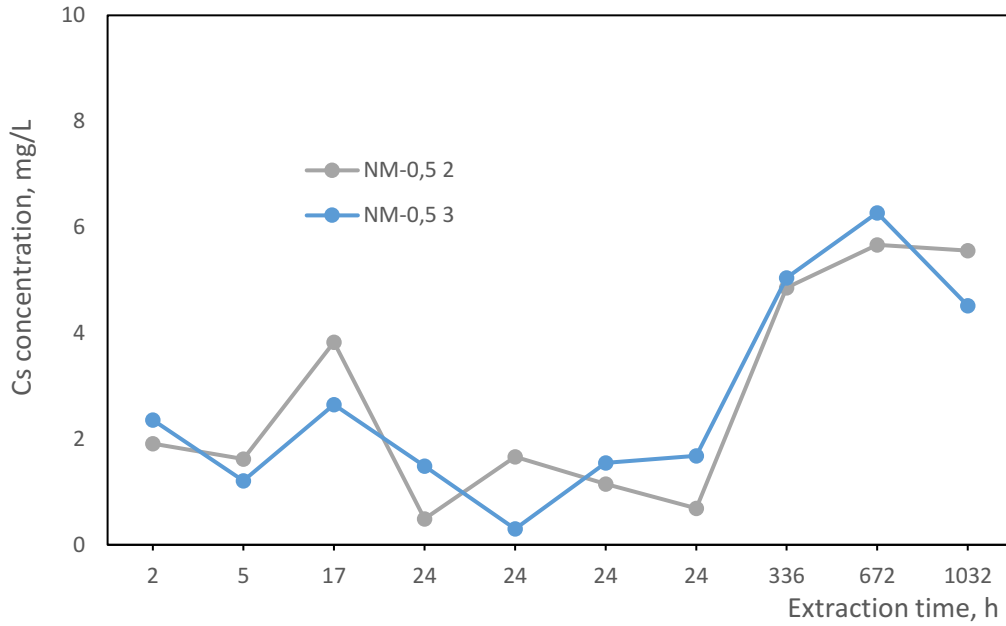


Figure 4.7. Concentration of Cs in group NM. Beam height was set to 4 mm, air flow rate 72 mL.min⁻¹, acetylene flow rate at 24 mL.min⁻¹. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

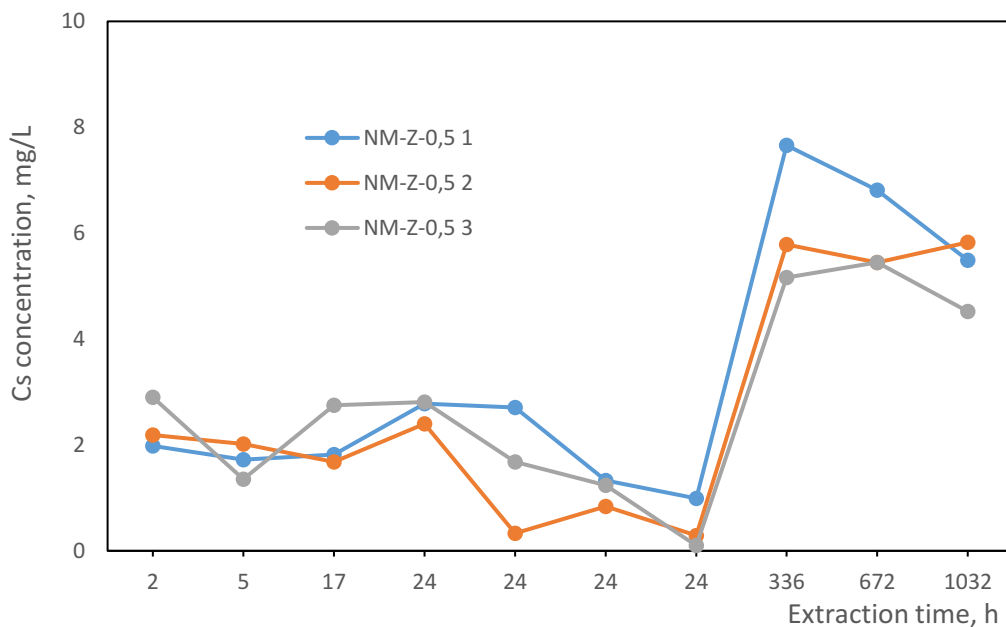


Figure 4.8. Concentration of Cs in group NM-Z. Beam height was set to 4 mm, air flow rate 72 mL.min⁻¹, acetylene flow rate at 24 mL.min⁻¹. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

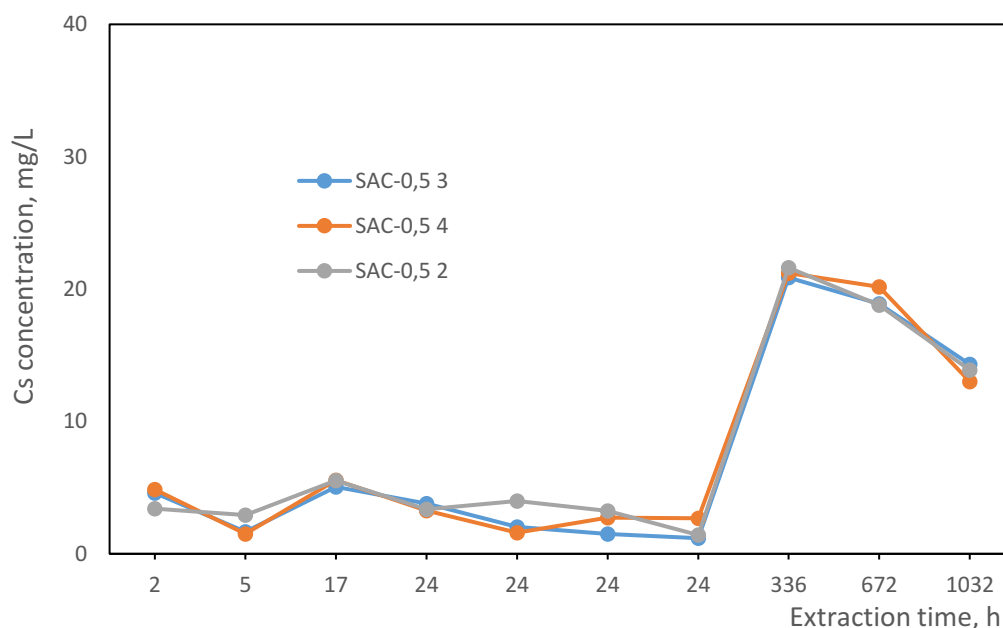


Figure 4.9. Concentration of Cs in group SAC. Beam height was set to 4 mm, air flow rate 72 mL.min⁻¹, acetylene flow rate at 24 mL.min⁻¹. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

4.5.2. Results of extracts with ionization buffer

In groups with added ionization buffer (figure 4.10., figure 4.11., figure 4.12., figure 4.13., figure 4.14., figure 4.15.), we can observe similar trends as without the addition of ionization buffer. Differences in concentration of Cs in some extracts (NP-0,5 3, NP-M-0,5 3, NP-M-0,5 2, NP-Z-0,5 2) could be explained by ionization of the analyte during measurement without the ionization buffer. This would prove the requirement of addition of ionization buffer.

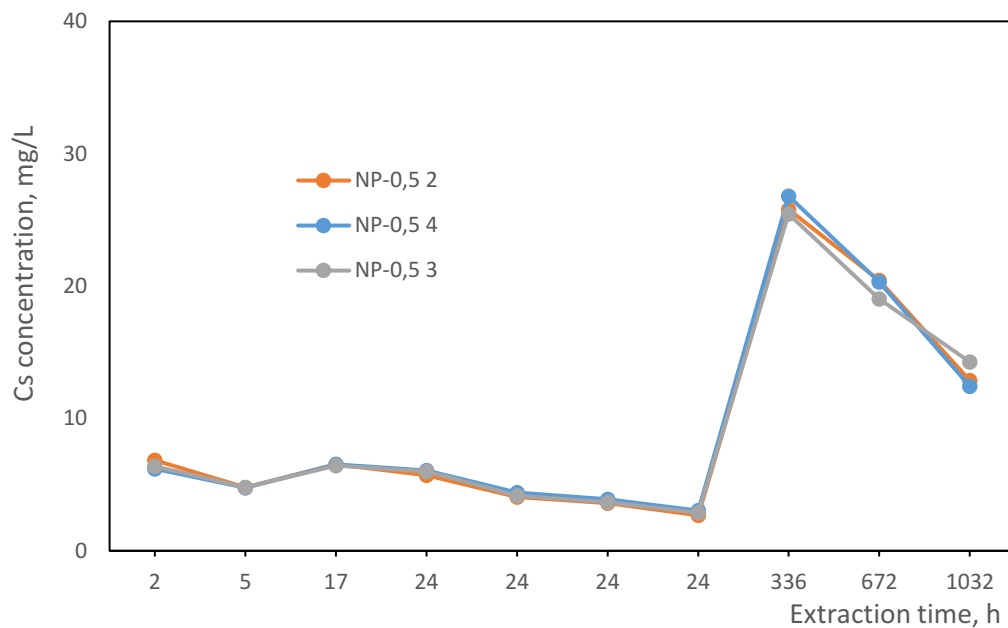


Figure 4.10. Concentration of Cs in group NP + KCl. Beam height was set to 4 mm, air flow rate $72 \text{ mL}\cdot\text{min}^{-1}$, acetylene flow rate at $24 \text{ mL}\cdot\text{min}^{-1}$. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

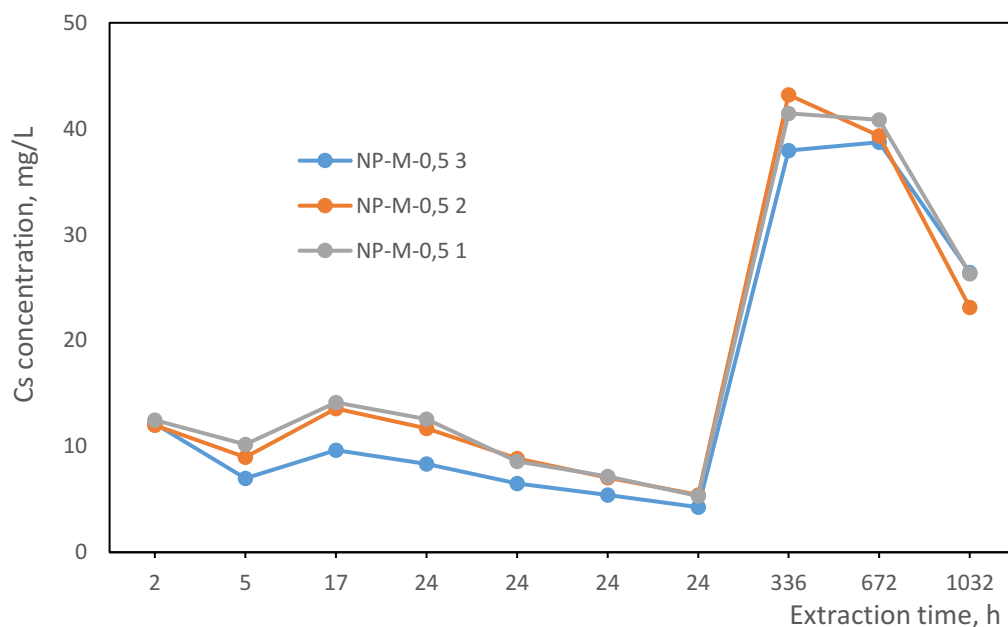


Figure 4.11. Concentration of Cs in group NP-M + KCl. Beam height was set to 4 mm, air flow rate $72 \text{ mL}\cdot\text{min}^{-1}$, acetylene flow rate at $24 \text{ mL}\cdot\text{min}^{-1}$. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

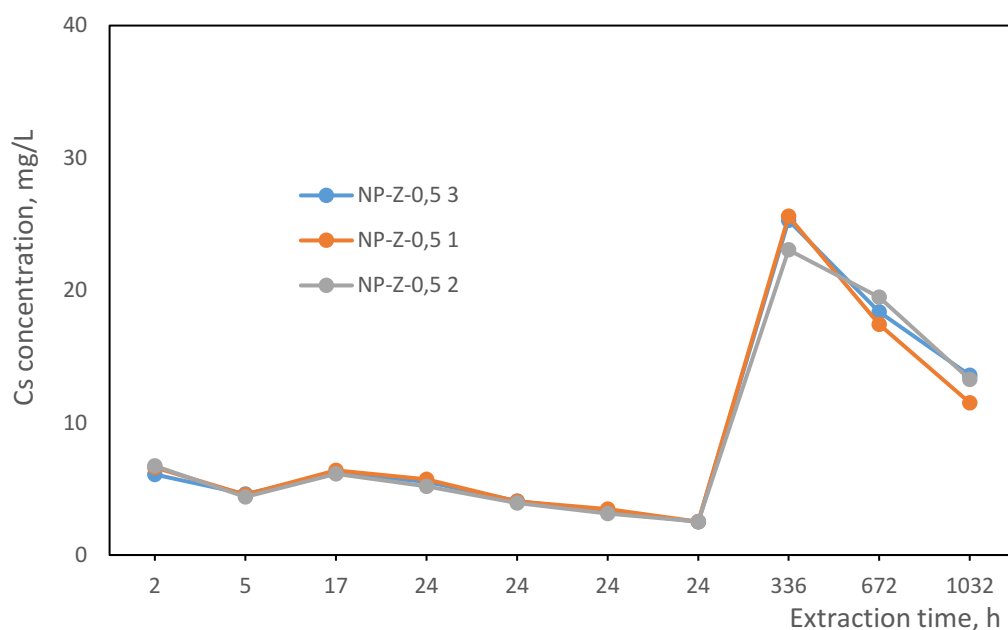


Figure 4.12. Concentration of Cs in group NP-Z + KCl. Beam height was set to 4 mm, air flow rate $72 \text{ mL}\cdot\text{min}^{-1}$, acetylene flow rate at $24 \text{ mL}\cdot\text{min}^{-1}$. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

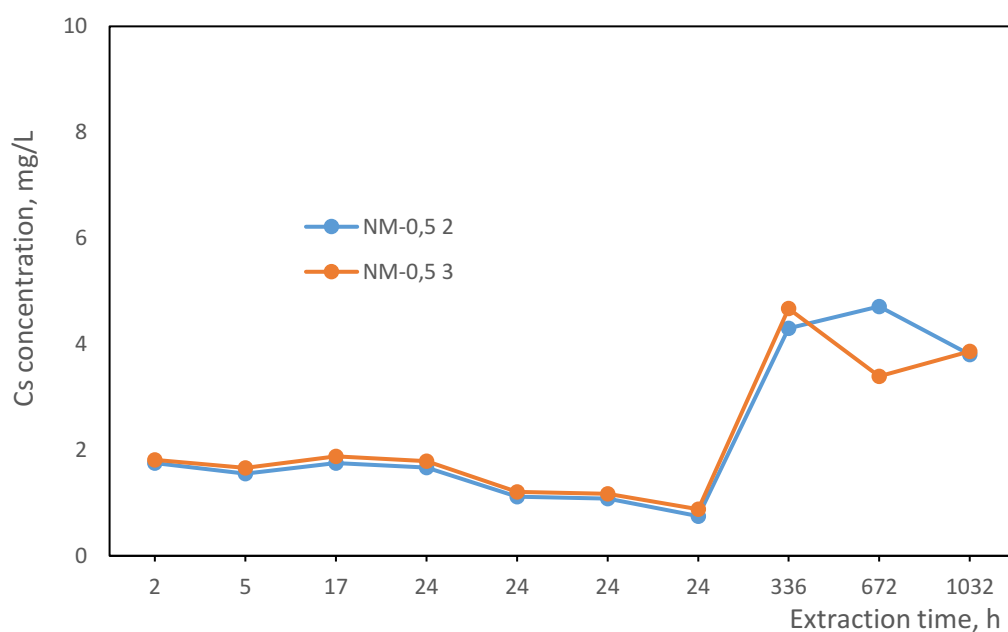


Figure 4.13. Concentration of Cs in group NM + KCl. Beam height was set to 4 mm, air flow rate $72 \text{ mL}\cdot\text{min}^{-1}$, acetylene flow rate at $24 \text{ mL}\cdot\text{min}^{-1}$. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

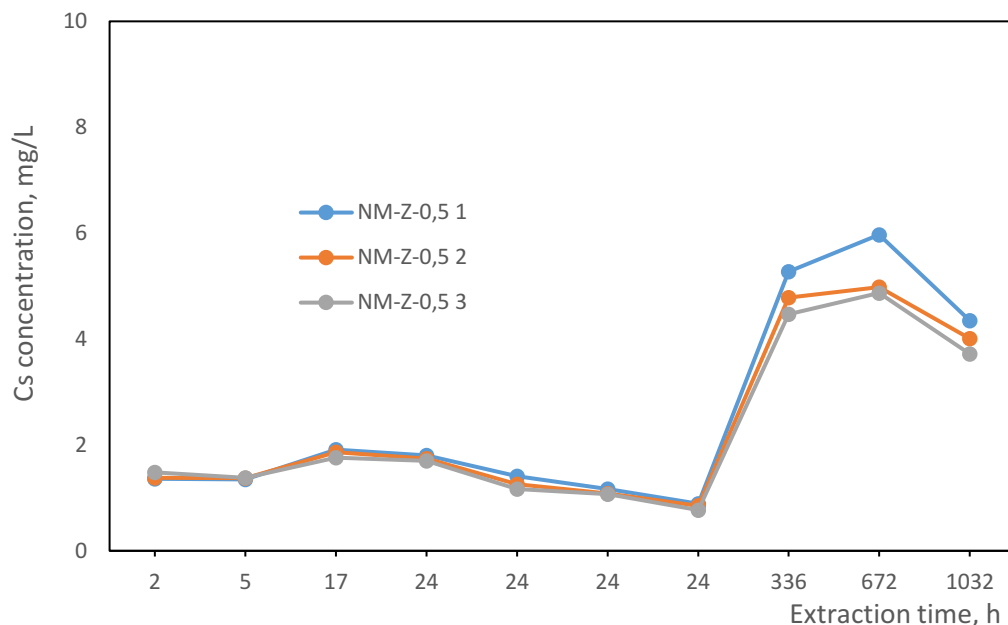


Figure 4.14. Concentration of Cs in group NM-Z + KCl. Beam height was set to 4 mm, air flow rate $72 \text{ mL}\cdot\text{min}^{-1}$, acetylene flow rate at $24 \text{ mL}\cdot\text{min}^{-1}$. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

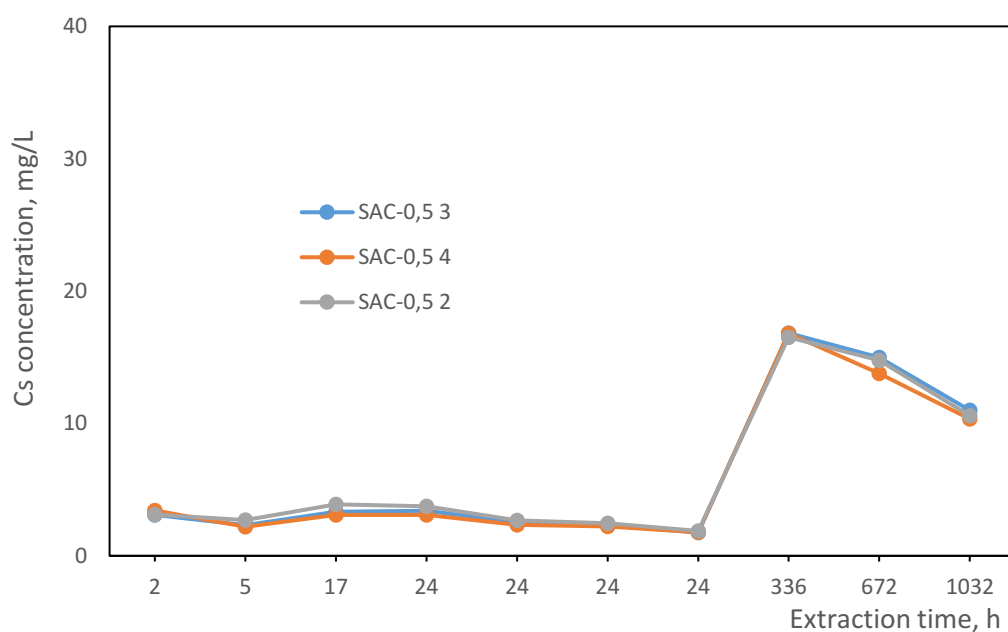


Figure 4.15. Concentration of Cs in group SAC + KCl. Beam height was set to 4 mm, air flow rate $72 \text{ mL}\cdot\text{min}^{-1}$, acetylene flow rate at $24 \text{ mL}\cdot\text{min}^{-1}$. HCl was operated at a lamp current of 15.0 mA and a wavelength of 852.1 nm.

5. Conclusions

17 cement samples were acquired from CTU as a model samples for radioactive waste, containing nonradioactive nuclides of Cs, widely used for waste storage in the ground. Out of each of the sample, 10 extractions with water were made, with extraction time ranging from 2 to 1036 hours. Influence of deionized or distilled water source on Cs concentration in extracts was questioned and dismissed. Cs content in these extracts was determined using F-AAS method, chosen for its suitability and practicality. Beam height and acetylene flow rate for F-AAS method for determination of Cs in water extracts was optimized. Optimal beam height was measured to be 4 mm and acetylene flow rate $25 \text{ mL}\cdot\text{s}^{-1}$. Limit of detection was calculated at $0.116 \text{ mg}\cdot\text{L}^{-1}$ and limit of quantification was determined $0.386 \text{ mg}\cdot\text{L}^{-1}$. Addition of ionization buffer to the extracts was explored and compared with results without the addition of ionization buffer, with differences found in concentration levels of some extracts, proving the need for addition of ionization buffer.

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