
EXPERIMENTAL TESTS FOR ^{36}Cl REMOVAL FROM AQUEOUS SOLUTION

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ABSTRACT

This paper presents the experimental tests of a chlorine separation and purification method from aqueous samples with knowing content of Co, Cs, Eu, Ni and Sr stable elements. The method is based on the property of chloride ions to form a silver chloride white precipitate, followed by the use of the extraction chromatography on the strong anionic resin (Bio-Rad AG[®] 1-X4) to purify chlorine. The concentrations of Co, Cs, Eu, Ni and Sr (separated from Cl by using precipitation method) were measured by ICP-OES. The silver chloride precipitate was dissolved in 25 % NH_3 solution and loaded onto the anionic resin. The chloride ions were strongly retained on the resin and eluted with a proper solution. The final solution, containing chloride ions, was converted to a form compatible with the spectrophotometric and Mohr titration techniques, which were used to determine chloride concentration. The separation yields of Co, Cs, Eu, Ni and Sr from Cl are very good. More than 98 % from the initial concentration of chlorine was recovered.

Key words: ^{36}Cl , separation, ion exchange resin

Introduction

The ^{36}Cl radioisotope is a pure β emitter ($E_{\text{max}} = 708.6$ keV) with a high importance in radioactive waste management due to its long half-life of 3.01E05 years and high mobility in the environment. Large amounts of ^{36}Cl have been released into the atmosphere and ocean waters by nuclear weapons testing. The ^{36}Cl radioisotope is produced in nuclear reactors by the neutron activation reaction $^{35}\text{Cl}(n, \gamma)^{36}\text{Cl}$, due to the presence of chlorine in many components (fuel elements, graphite, construction materials, cooling water) [1].

Measurement of ^{36}Cl radioactivity is based on detection of its beta particles emission which requires a chemical separation from other interfering radionuclides. ^{36}Cl concentration in wastes is generally much lower than other radionuclides concentration; therefore further purification to separate ^{36}Cl from other interfering radionuclides is necessary [1].

Experimental

The separation and purification method of ^{36}Cl was developed on standard samples of appropriate concentrations for the ICP-OES analysis, prepared by combining and diluting calibration standard solutions of 1000 mg/L (Co, Cs, Eu, Ni and Sr stable elements) and sodium chloride (the stable isotope of chlorine with the same properties with ^{36}Cl was used).

Chemical separation of Co, Cs, Eu, Ni and Sr from Cl

The removal method of interfering elements (Co, Cs, Eu, Ni and Sr) from sample is based on the property of chloride ions to precipitate in presence of silver nitrate solution. **Figure 1** shows the flow diagram of the applied method for chemical separation of Co, Cs, Eu, Ni and Sr from Cl.

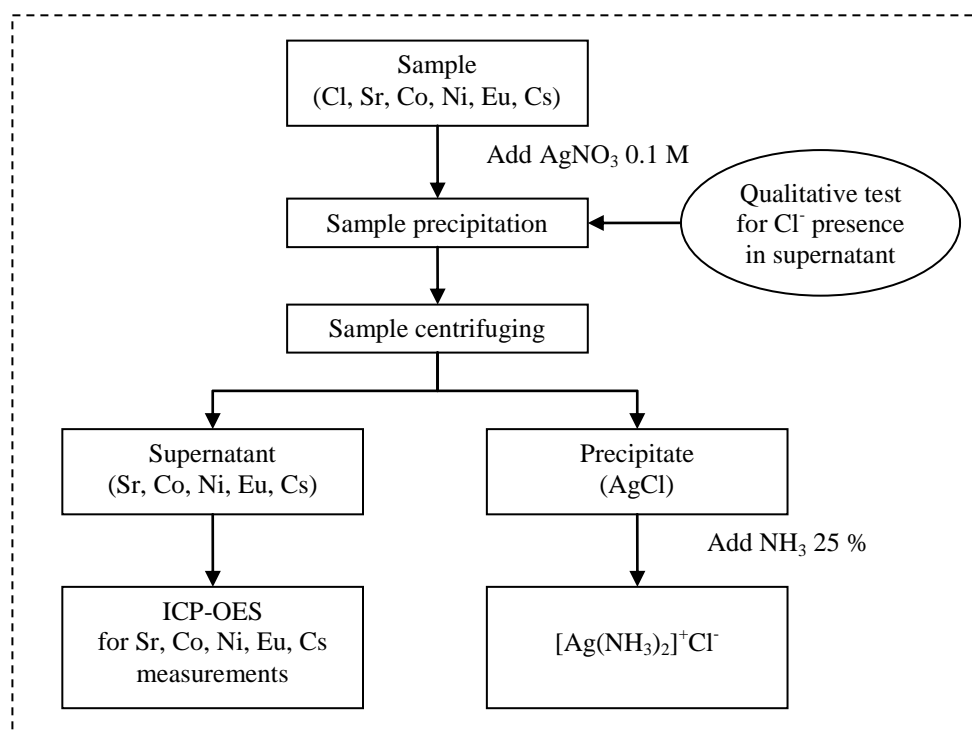


Figure 1 Flow diagram of the separation method for Co, Cs, Eu, Ni and Sr

Chemical purification of chlorine

A column sorption-elution study was carried out by using a Bio-Rad AG[®] 1-X4 resin of 50-100 mesh. This resin is a strongly basic anion exchanger with quaternary ammonium functional groups attached to the styrene divinylbenzene copolymer lattice. The resin is supplied in the chloride form by Bio-Rad Laboratories [2]. The selective separation of Cl is obtained by converting the resin to nitrate form. **Figure 2** shows the flow diagram of the proposed method for ^{36}Cl purification from aqueous samples.

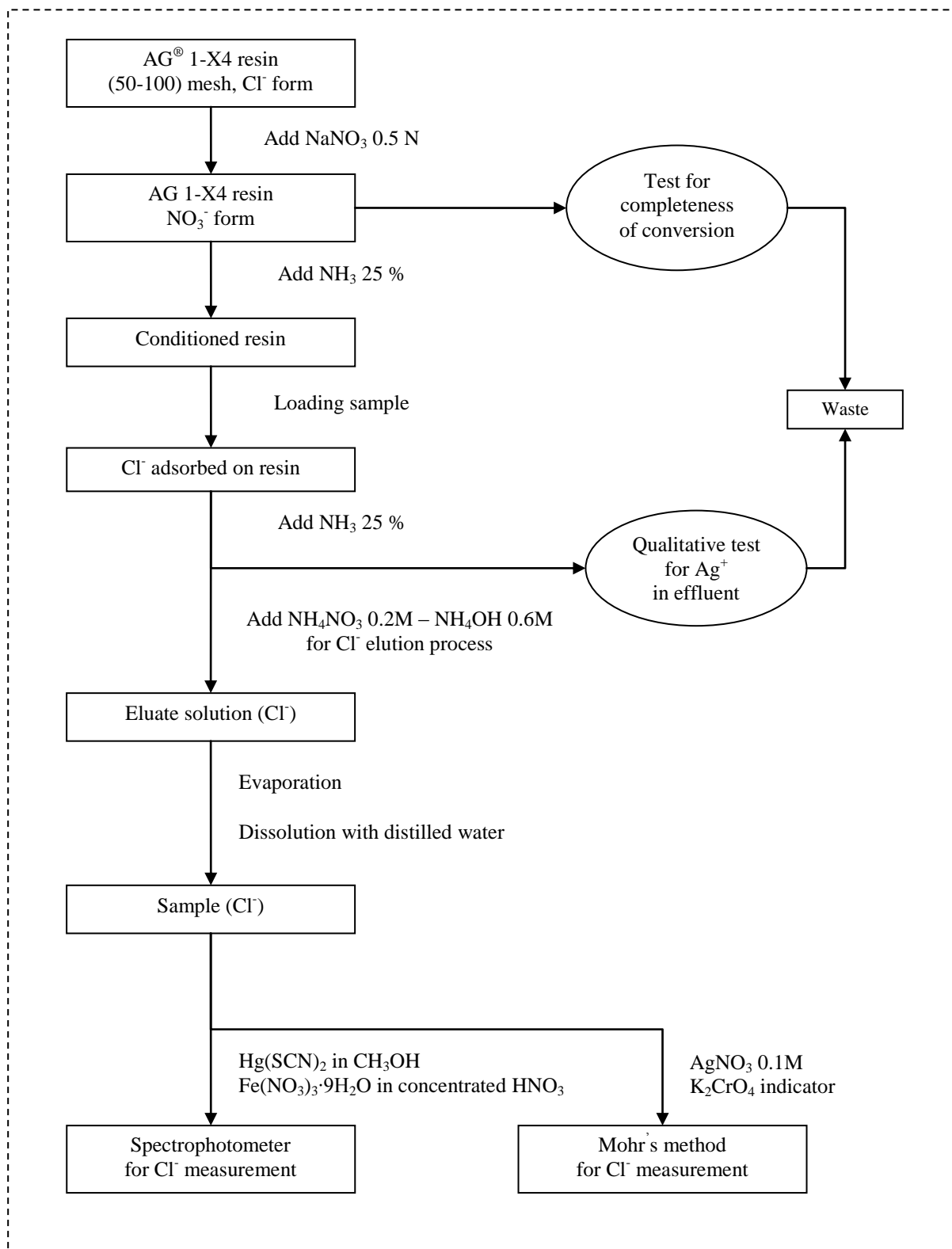


Figure 2 Flow diagram of the purification method for chlorine

Results and discussion

Assessment of Co, Cs, Eu, Ni and Sr concentrations in supernatant sample (C_f) was achieved using calibration curves [3-4] for Co, Cs, Eu, Ni and Sr. ICP-OES was also used to measure the initial concentration (C_i) of stock solution (**Table 1**). The separation yields of Co, Cs, Eu, Ni and Sr from Cl are very good (**Table 2**).

Table 1 Co, Cs, Eu, Ni and Sr concentrations in the initial and supernatant samples

Element	C_i [mg/L]	Stddev [mg/L]	RSD [%]	C_f [mg/L]	Stddev [mg/L]	RSD [%]
Co	7.761	0.01300	0.1675	7.688	0.06609	0.8596
Cs	8.423	0.07668	0.9103	8.449	0.13940	1.6500
Eu	7.894	0.01388	0.1758	7.798	0.06215	0.7970
Ni	7.942	0.02441	0.3073	8.083	0.01502	0.1858
Sr	7.739	0.02630	0.3399	7.659	0.09536	1.2450

Table 2 Results of the experimental test for separation method of Co, Cs, Eu, Ni and Sr from Cl

Element	Separation yield [%]
Co	99.060 ± 1.735
Cs	100.309 ± 3.781
Eu	98.784 ± 1.612
Ni	101.775 ± 0.731
Sr	98.966 ± 2.554

The reported uncertainty is an expanded uncertainty as defined in the International Vocabulary of Metrology [5], calculated using a coverage factor of 2, which gives a level of confidence of approximately 95%.

To evaluate the recovery yield of chlorine achieved by the chemical separation and purification procedure, spectrophotometric (thiocyanate-iron method) and titration methods were applied.

In spectrophotometric method [6-7], chloride ions substitute the thiocyanate ions in undissociated mercury thiocyanate. The released thiocyanate ions react with ferric ions forming a red iron-thiocyanate complex.

The Mohr's method [8] determines the chloride ion concentration of a solution by titration with silver nitrate when a precipitate of silver chloride forms. A volume of 2.81 mL 0.1 N AgNO₃ solution is necessary to achieve equivalent point for 40 mL sample containing chloride ions (**Figure 3**).

The results obtained from the analysis (spectrophotometric and titration methods) are shown in **Table 3**.

Table 3 Results of the experimental tests for separation and purification method of Cl

Method	m_{Cl} [mg]		Recovery [%]
	Initial	Final	
Spectrophotometry	25.00 ± 0.0008	24.53 ± 0.1815	98.12 ± 0.73
Titration	25.00 ± 0.0008	24.64 ± 0.2593	98.56 ± 1.04

m_{Cl} – mass of chloride ions separated by precipitation – ionic exchange chromatography.
The reported uncertainty is an expanded uncertainty as defined in the International Vocabulary of Metrology [5], calculated using a coverage factor of 2, which gives a level of confidence of approximately 95%.

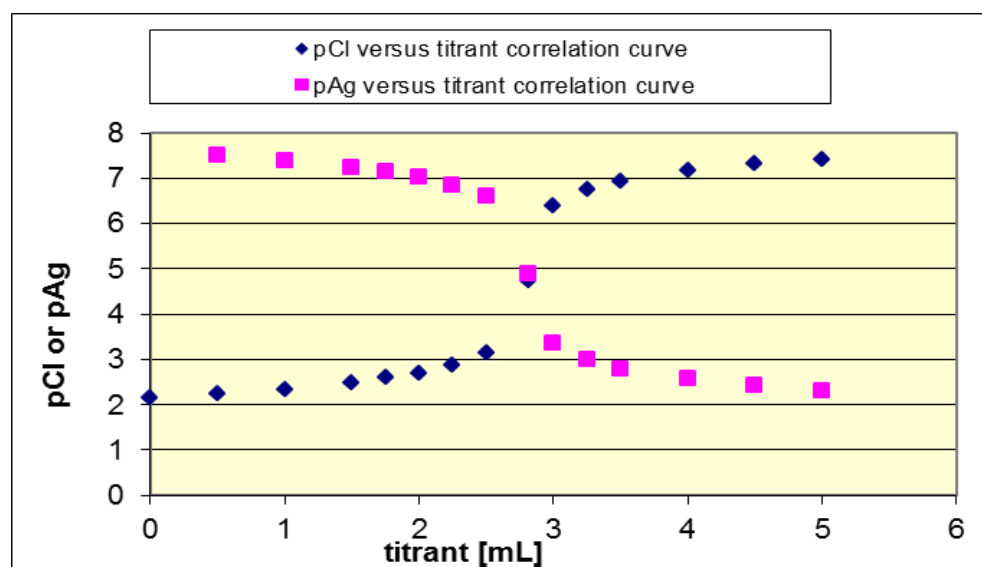


Figure 3 Titration curve of 40 mL Cl^- solution with 0.1 N $AgNO_3$ solution

Conclusion

The applied methodology allowed the Co, Cs, Eu, Ni, Sr separation and the Cl purification. The separation method of the interfering elements (Co, Cs, Eu, Ni and Sr) was efficiently achieved by using the precipitation of chloride ions. For the Cl purification, Bio-Rad AG[®] 1-X4 strong anionic resin was used due to its ability to retain chloride ions from aqueous solutions.

References

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