

A comparative study on the influence of the type of acid used for ^{55}Fe and ^{63}Ni determination in steel samples through Liquid Scintillation Counting

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Abstract In decommissioning of nuclear facilities the presence of activated steel requires the determination, along with other radionuclides, of ^{55}Fe and ^{63}Ni . These can be considered as hard-to-measure-radionuclides because of their low energy beta particles or X radiation emitted. Furthermore, those radionuclides are usually mixed with a relevant fraction of non-radioactive Fe and Ni. This implies that, in those cases involving very low radioactive samples close to background activity level, a significant mass of steel sample must be physically and chemically treated and analyzed to achieve the Minimum Detectable activity Concentration (MDC) required by the Authority for clearance purposes. Due to colour quenching the acquisition time is particularly long. Minimizing the colour effect is therefore important for laboratories that must perform many determinations in a reasonable time, achieving the MDC in accordance with the Authority requests. For this reason, the choice of solvent can be an important information to save analyses time. The intensity of the colour quenching is, in fact, strongly dependent on the type of acid used to solubilize the sample before the mixing with the liquid scintillation cocktail. Some types of acid can even increase the phenomenon while others can drastically reduce such an effect. The aim of this work is to offer, through a correlation study between sample concentration in the LSC vial and type of solvent used in dilution, a reliable method for quantifying ^{63}Ni and ^{55}Fe in steel samples with very low activity, close to the background level.

Keywords —Liquid Scintillation Counting, decommissioning of nuclear installations, neutron activated steel.

I. INTRODUCTION

Decommissioning of nuclear fission and fusion facilities leads to production, among others, of waste including activated steel. Among the most occurring radionuclides, neutron activation of steel could cause the production of gamma emitter radionuclides (e.g., ^{54}Mn , ^{58}Co , ^{60}Co) along with ^{55}Fe and ^{63}Ni , which can be considered as hard-to-measure-radionuclides because of their low energy beta particles or X radiation emitted. Both ^{63}Ni and ^{55}Fe are neutron activation products. ^{63}Ni mainly exists in steel because of the high concentration of Ni in these materials. It is a pure beta emitting

radionuclide with maximum beta energy of 66.95 keV and half-life of 100.1 years. Due to its low beta energy, the measurement by gas flow proportional counter gives low counting efficiency (2.6–20%) [1].

Fe is produced by neutron activation reactions of two major stable iron isotopes: ^{54}Fe (n, γ) ^{55}Fe and ^{56}Fe ($n, 2n$) ^{55}Fe . Iron is the steel main component, and its concentration is relatively high in several reactor materials [2]. In the first few years after reactor operation has stopped ^{55}Fe is a main contributor to the radioactivity of nuclear waste. ^{55}Fe ($t_{1/2} = 2.7$ years) decays via electron capture to stable ^{55}Mn with the emission of Auger electrons and low energy X-rays (5.89 keV, 16.9%). Measurement of ^{55}Fe can be carried out by low energy gamma and X-ray detector or gas flow proportional counter, but their counting efficiencies are usually very low (< 1%) [2].

For reaching higher detection efficiencies and lower MDC in ^{55}Fe and ^{63}Ni determination, Liquid Scintillation Counting (LSC) is the most suitable technique, but it requires a chemical separation which produces strongly coloured ^{63}Ni and ^{55}Fe fractions inevitably mixed with non-radioactive Ni and Fe, still present into the materials in high mass percentage. LSC technique is very sensitive to colour quenching effect, which occurs when coloured substances, present in the sample, absorb the light emitted by scintillator before it can escape the vial and reach the photomultipliers. Therefore, minimizing the colour effect is important for laboratories that must carry out many measurements, often close to background activity level, in a reasonable time for achieving the MDC in accordance with the Authority requirements. When MDC is particularly low, a large amount of steel sample must be physically and chemically treated and, due to the colour quenching and efficiency reduction, the acquisition time is consequently dramatically increased. To save analysis time, the choice of solvent can be very important. The intensity of the colour quenching is, in fact, strongly dependent on the type of acid used to solubilize the sample before mixing with the liquid scintillation cocktail. Some types of acid can even increase the phenomenon while others can drastically reduce the effect. The aim of this work is to offer, through a correlation study between sample concentration in the LSC vial and type of solvent used in dilution, a reliable method for quantifying ^{63}Ni and ^{55}Fe in steel sample with very low activity level, close to the background. To do this, many samples by simulating the amount of Fe and

Ni contained in a steel AISI 304L (Fe = 69.06% w/w, Ni = 9.25% w/w) were prepared and dissolved in 5 different acids. Coordination chemistry is the basic chemistry of metal ions which receive electron pairs from ligands around it. Several approaches have been adopted to reduce the intensive colour quench of Fe (solvent extraction [3] or treatment by reducing agents [4]), but it has not been possible to overcome this effect completely, because the reduced Fe²⁺ is not very stable. Nickel is one of transition metals and abounds in nature as nickel (II) because more stable than nickel (0), nickel(I), nickel (III), and nickel (IV). Its salts are commonly green due to the presence of hexa aquanickel(II) ion [Ni (H₂O)₆²⁺]. Chemistry of iron aqueous solution is based on two oxidation states, Fe²⁺ and Fe³⁺. Both forms are thermodynamically stable and kinetically reactive [7]. Their compounds can take a wide range of colours depending on the oxidative state.

II. MATERIALS AND METHODS

Iron chloride (FeCl₃), nickel chloride (NiCl₂), hydrochloric acid (HCl), phosphoric acid (H₃PO₄), nitric acid (HNO₃), phosphonic acid (H₃PO₃), sulfuric acid (H₂SO₄) and sulfurous acid (H₂SO₃) are considered in this work, along with radioactive standard solutions of ⁶³Ni and ⁵⁵Fe. 24 samples, containing iron and nickel in the same proportion as AISI 304L and different concentrations, were prepared starting from iron chloride and nickel chloride and dissolved respectively in HCl, H₃PO₄, HNO₃, H₃PO₃, H₂SO₃ and H₂SO₄ (Fig.1 – phase 1). The prepared samples simulate iron and nickel fractions resulting from chromatographic separation. For this reason, the two elements were studied separately, 24 samples simulating the iron fraction and 24 samples simulating the nickel fraction were prepared.

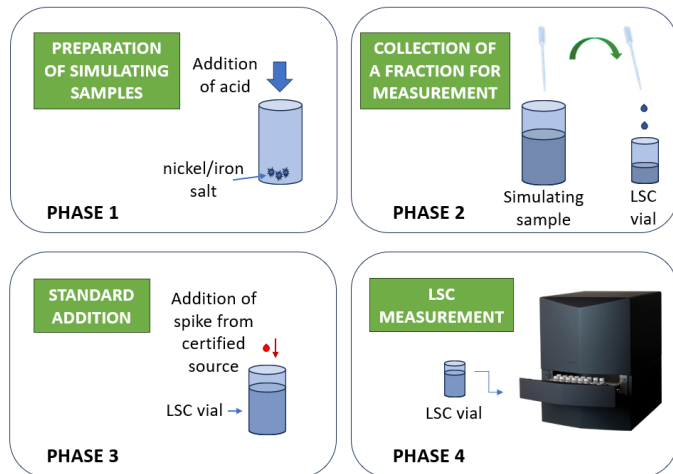


Fig. 1 Phases for sample preparation and analysis

Different fractions of each simulating sample were then collected in LSC vials varying sample concentration to evaluate the measurement performances in terms of LSC efficiency and acquisition time needed for reaching the required MDC (Fig.1 – phase 2). A LSC analysis was performed on all the vials before the internal standard calibration to evaluate the blank contribution.

To each vial, a known amount of ⁵⁵Fe (17 ± 1 Bq) and ⁶³Ni (34 ± 2 Bq) standard were finally added for calibration (Fig.1 – phase 3). For the radiometric measurements of ⁵⁵Fe and ⁶³Ni, a Hidex 300 SL automated system was used and LSC efficiency was evaluated (Fig.1 – phase 4).

Based on previous chemical purification experiences in recovering Fe and Ni, an average chemical yield of (60±6) % for each element was assumed and the needed acquisition time was calculated from Currie [5] fixing MDC to 0.3 Bq/g. Uncertainty evaluation on iron and nickel masses and on LSC efficiencies was based on the propagation of uncertainties related to each variable involved (Fig.2-3).

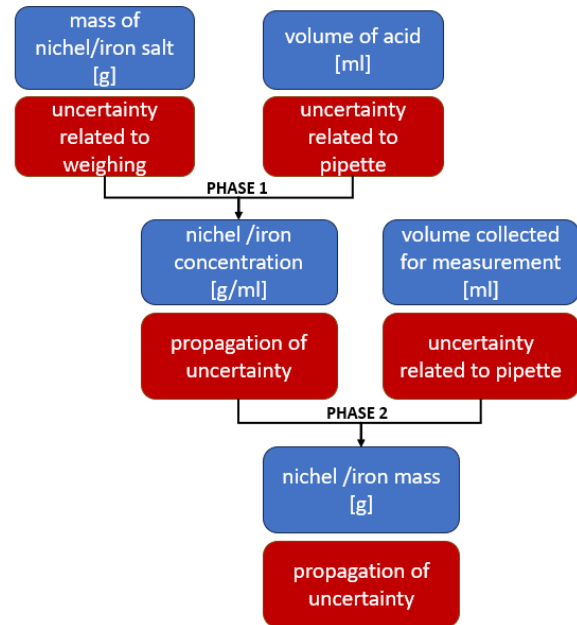


Fig. 2 Uncertainty propagation for nickel/iron mass evaluation

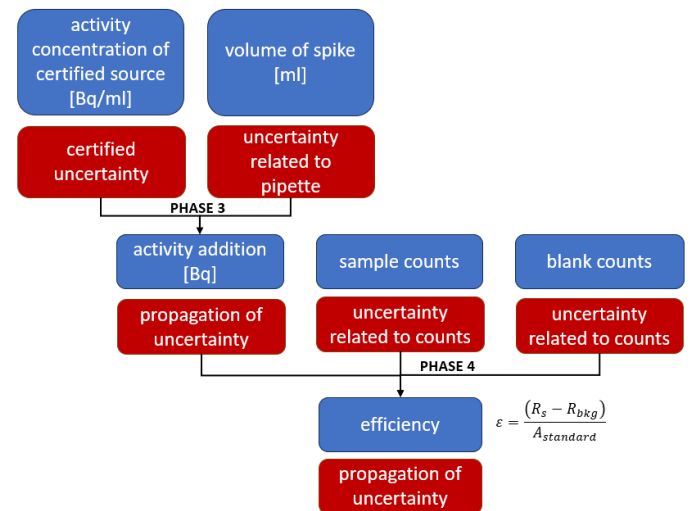


Fig. 3 Uncertainty propagation for efficiency evaluation. R_s is the counting rate related to spiked sample, R_{bkg} is the counting rate related to blank sample, $A_{standard}$ is the activity added as standard for calibration.

III. RESULTS

The results in term of LSC efficiency and acquisition time for ⁵⁵Fe and ⁶³Ni determination are reported in Tables I-II. Empty cells indicate that under this condition the efficiency is too low

to be evaluated: colour quenching effect is too intense, or more phases or a milky solution appeared (Fig.4).

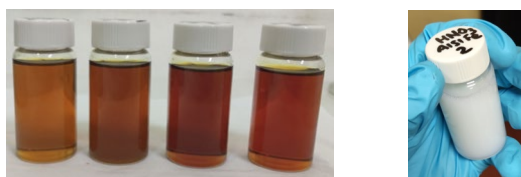


Fig. 4 colour and immiscibility effects

TABLE I

EFFICIENCY AND ACQUISITION TIME FOR ⁵⁵Fe DETERMINATION

Acid	Conc. Molar	Fe mass (mg)	LSC eff. %	acq. Time (days)
HCl	2	21.5±0.2	8.2±0.3	879.1
		43.0±0.4	3.5±0.2	1194.1
		86.0±0.9	0.9±0.1	4738.0
		172.0±1.7		
H ₂ SO ₃	0.375	21.5±0.2		
		43.0±0.4		
		86.0±0.9		
		172.0±1.7		
H ₂ SO ₄	2	21.5±0.2	30.2±1.1	75.3
		43.0±0.4	21.5±0.8	35.1
		86.0±0.9	4.4±0.2	188.3
		172.0±1.7		
H ₃ PO ₃	1	21.5±0.2	38.8±1.4	43.5
		43.0±0.4	36.1±1.3	12.7
		86.0±0.9	33.6±1.2	3.5
		172.0±1.7	27.4±1.0	1.3
H ₃ PO ₄	2	21.5±0.2	37.2±1.4	48.2
		43.0±0.4	37.7±1.4	11.6
		86.0±0.9	34.0±1.3	3.5
		172.0±1.7	28.1±1.0	1.3
HNO ₃	2	21.5±0.2		
		43.0±0.4		
		86.0±0.9		
		172.0±1.7		

TABLE II

EFFICIENCY AND ACQUISITION TIME FOR ⁶³Ni DETERMINATION

Acid	Conc. Molar	Ni mass (mg)	LSC efficiency %	acq. time (hours)
HCl	2	6.0±0.1	67.8±4.4	161.4
		12.0±0.1	65.8±4.3	42.5
		24.0±0.2	62.6±4.1	11.1
		36.0±0.4	60.1±3.6	5.4
H ₂ SO ₃	0.375	6.0±0.1		
		12.0±0.1		
		24.0±0.2		
		36.0±0.4		
H ₂ SO ₄	2	6.0±0.1	68.8±4.4	157.1
		12.0±0.1	67.9±4.4	41.2
		24.0±0.2	65.4±4.3	11.0
		36.0±0.4	63.6±4.2	5.1
H ₃ PO ₃	1	6.0±0.1	67±4.4	163.5
		12.0±0.1	65.5±4.3	42.7
		24.0±0.2	62.3±4.0	12.0
		36.0±0.4	59.1±4.0	5.7
H ₃ PO ₄	2	6.0±0.1	69.0±4.5	155.4
		12.0±0.1	67.2±4.4	40.0
		24.0±0.2	64.0±4.2	10.8
		36.0±0.4	61.5±4.1	5.3
HNO ₃	2	6.0±0.1	63.0±4.1	188.1
		12.0±0.1	60.8±3.9	49.8
		24.0±0.2	56.1±3.7	14.2
		36.0±0.4	52.7±3.6	7.4

Correlation between mass, type of solvent and efficiency is shown. The associated uncertainty has been calculated following the scheme in Fig.2-3. The aspect of vials for increasing iron or nickel mass concentration and for different types of acid is shown in Tables III-IV.

TABLE III
ASPECT OF VIALS FOR ⁵⁵Fe DETERMINATION


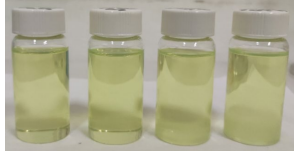




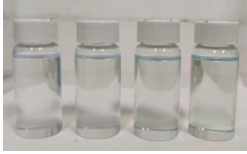
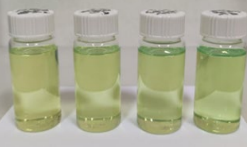

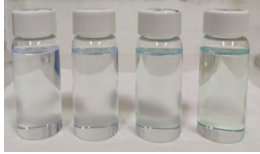

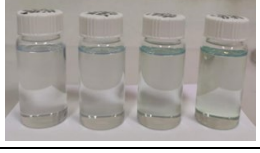
Acid	Conc. Molar	Fe mass (mg)	
HCl	2	21.5±0.2	
		43.0±0.4	
		86.0±0.9	
		172.0±1.7	
		21.5±0.2	
H ₂ SO ₃	0.375	43.0±0.4	
		86.0±0.9	
		172.0±1.7	
		21.5±0.2	
		43.0±0.4	
H ₂ SO ₄	2	86.0±0.9	
		172.0±1.7	
		21.5±0.2	
		43.0±0.4	
		86.0±0.9	
H ₃ PO ₃	1	172.0±1.7	
		21.5±0.2	
		43.0±0.4	
		86.0±0.9	
		172.0±1.7	
H ₃ PO ₄	2	172.0±1.7	
		21.5±0.2	
		43.0±0.4	
		86.0±0.9	
		172.0±1.7	
HNO ₃	2	43.0±0.4	
		86.0±0.9	
		172.0±1.7	
		21.5±0.2	
		43.0±0.4	

TABLE IV
ASPECT OF VIALS FOR ⁶³Ni DETERMINATION

Acid	Conc. Molar	Ni mass (mg)	
HCl	2	6.0±0.1	
		12.0±0.1	
		24.0±0.2	
		36.0±0.4	
		6.0±0.1	
H ₂ SO ₃	0.375	12.0±0.1	
		24.0±0.2	
		36.0±0.4	
		6.0±0.1	
		12.0±0.1	
H ₂ SO ₄	2	24.0±0.2	
		36.0±0.4	
		6.0±0.1	
		12.0±0.1	
		24.0±0.2	

H ₃ PO ₃	1	6.0±0.1	
		12.0±0.1	
		24.0±0.2	
		36.0±0.4	
		6.0±0.1	
H ₃ PO ₄	2	12.0±0.1	
		24.0±0.2	
		36.0±0.4	
		6.0±0.1	
		12.0±0.1	
HNO ₃	2	24.0±0.2	
		36.0±0.4	
		6.0±0.1	
		12.0±0.1	
		24.0±0.2	

IV. DISCUSSION

In many cases vials containing iron fractions are coloured of different yellow levels. Several approaches have been adopted in literature to reduce the colour quench of iron, such as solvent extraction [3,6] and reduction of Fe³⁺ to Fe²⁺ by ascorbic acid [4]. It has not been possible to overcome the colour quench of iron completely, because the reduced Fe²⁺ is not very stable and it will be oxidized to Fe³⁺ very slowly. The most common acid used in LSC is HCl: it shows a high range sample uptake (only water is better) and the lowest misclassification range, but in the case study the results with HCl display unsatisfactory performances and other acids can be more suitable for a reliable LSC measurement such as H₃PO₃ and H₃PO₄. The solutions obtained with those acids are colourless for both iron and nickel solutions and provide the best performances in terms of efficiency and acquisition time. Instead, the iron solutions in HCl are coloured causing the worsening of outgoing efficiency values. Among the wide range of results, this study confirms for ⁵⁵Fe determination what is reported in [8] and [2] regarding the possibility to use H₃PO₄ to decolourize Fe³⁺ solutions and the behaviour of HNO₃ as a high quenching agent that can significantly reduce the counting efficiency.

In most cases, vials containing nickel fraction are weakly coloured of green. The resulting colour quenching affects the LSC efficiency in a similar way for all the type of acids except for H₂SO₃, whose corresponding solutions are strongly coloured and produce very low counting rates not discriminable from the background level. Some hours are sufficient for acquiring data for ⁶³Ni determination in accordance with Authority request respect to days needed for ⁵⁵Fe.

V. CONCLUSION

As a chromatographic purification is required to separate iron and nickel from the radioactive steel matrix, the purpose of this study is to offer an overview on the influence of different types of elution solvent on some of the LSC key parameters (i.e., sample concentration in the LSC vial, detection efficiency, quenching effect) to minimize the acquisition time needed to reach the MDC when the activity levels are lower than the unconditional release level and the materials are expected to be recycled or reused. HCl and HNO₃ are the most used acids in

^{55}Fe / ^{63}Ni isolation [3], but the results showed in Table I provide evidence that H_3PO_3 or in H_3PO_4 might be suitable alternatives for efficiently dissolving iron samples. Nickel fractions display a common behaviour towards a wider range of acids (except for H_2SO_3), showing only small variation in the considered parameters.

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