DETERMINATION OF LOW LEVEL C, S, SI AND P IN FERRITIC STEELS

Background

Many essential properties of ferritic steels commonly used in the nuclear industry are known to depend on the presence and the concentration of alloying elements and impurities. The resistance to corrosion and the susceptibility to embrittlement are two examples among several other characteristics governing the evolution of the mechanical and chemical properties of the steels submitted to irradiation in the long term. Under particular conditions, segregation effects may also happen e.g. as a result of thermal treatments or during welding, or simply by ageing, thereby affecting the local properties of the material. Therefore, the surveillance of the material integrity relies not only on the examination of the microstructure, but also on the precise analytical determination of low concentrations of key chemical components. However, such determinations are often complicated by the nature of the matrix. Whatever the analytical technique being used, interferences are likely to play an adverse role affecting the detection limit of the method as well as the accuracy and the precision of the results.

Objectives

We aimed to qualify and implement specific analytical techniques for the determination of low concentrations of four elements, namely C, S, Si and P in ferritic steels. In the framework of a contract with an external client, we had to respect the constraints reported in the table hereafter.

Targeted element	Expected range of concentration (wt. %)	Expected precision 1 σ for given concentration (wt. %)
Si	0.40 – 0.75	0.01
P	0.015 – 0.030	0.001
C	0.05 – 0.10	0.005
S	0.020 – 0.040	0.001

Constraints as imposed by contractual agreement

Principal results

The determination of low concentrations of silicon

Most standardised methods rely on the colorimetric measurement of a partially reduced silicododecamolybdate absorbing light at 820 nm. Unfortunately, many interferences affect this technique since several other chemical elements (As, Bi, P, Ge, Sb etc.) form similar heteropolyacids with molybdates, all absorbing light between ~800 and ~850 nm. Therefore, we opted for an electrochemical selective detection of the silicododecamolybdate, after having adapted the procedure to ensure the full and fast conversion of all silicon species into the said heteropolyacid. The achievements are as follows:

- we optimised the make-up of the complex: we found experimental conditions under which other species would not interfere as long as their concentrations do not exceed specific thresholds. In particular, a molar P/Si ratio up to 40 does not impair the result;
- we discovered also a catalyst acting efficiently on the complex formation, thereby reducing the reaction time down to 7 minutes;
- we tuned finely all electrochemical variables. The effective measurement consists in carrying out a DPASV (Differential Pulse Anodic Stripping Voltammetry) on a hanging mercury drop electrode;
- we wrote a VBA (Visual Basic Application) code to efficiently separate the faradic response from the baseline, thereby facilitating the data treatment in routine operation;
- we validated the method using 5 ASTM certified standard steels. Both the accuracy and the precision were found to be better than 12 % relative to the mean values. We adapted the method to cope with the expected range of concentration as mentioned by our client. Using the present set-up, the detection limit is around 0.005 wt. % of Si in the original sample;
- the calibration remains linear up to at least 200 ng $Si.mL^{-1}$ in the measuring cell.

The method can be adapted to the detection of much lower concentrations. Taking advantage of the favourable stoichiometry of the complex (Si : Mo = 1 : 12) and of the perspectives offered by DPASV, the detection limit may be reduced down to 0.0001 wt. % Si in the sample.

The determination of low concentrations of C and S

We carried out exploratory research, thereby identifying several possible techniques. Considering the fast production of quality results at the expense of minimal routine operation work, we opted for a standardised method based on the full combustion of the sample in a tubular oven under an oxygen stream. According to the manufacturer, the addressable concentration ranges are 10 ppm to 100 wt. % for C and 10 ppm to 10 wt. % for S, depending on the weight of the sample, the claimed accuracy being better than 2 % relative to the mean values. Using this equipment, we carried out the following tasks:

- we validated the technique, using 5 ASTM standard steels. The practical detection limits appear to be 100 ppm for both C and S. The precision was better than 5 % for C and better than 10 % for S. However, we observed a slight lack of accuracy in some circumstances. This led us to formulate appropriate recommendations, especially regarding the sample preparation and the regulation of ambient temperature;
- we carried out the successful measurement of samples of unknown composition delivered by our client;
- we examined the perspective of applying the method to Ni-base alloys.

The determination of low concentrations of P

The case of P is pretty similar to the case of Si. Most standardised methods rely on the colorimetric determination of a heteropolyacid complex formed by reaction with ammonium molybdate. Again, we opted for a selective electrochemical detection of the P containing complex. However, the observed response is now related to the change of the double layer capacitance caused by the adsorption of the complex on a hanging mercury drop electrode. The current wave is observed during a fast CV (Cyclic Voltammetry) scan at 250 $mV.s^{-1}$. Appropriate research work yielded the following achievements:

- we optimised the make-up of the complex: we found experimental conditions under which interferences are minimised;
- we tuned all electrochemical variables. The effective measurement consists in carrying out a fast CV on a hanging mercury drop electrode;
- we wrote a VBA (Visual Basic Application) code to separate the adsorptive response from the baseline;
- we validated the method using 1 ASTM certified standard steel. Further validation work is now running.

So far, two methods have been implemented for the determination of three elements (Si, C and S). The P measurement technique still requires further tuning prior to reach its final development stage. The main characteristics of the methods are given in the table below.

Element	Range of applicability (wt. %)	Precision 1 σ for mid-range concentration (wt. %)	Detection limit (wt. %)
Si	0.005 - 1	0.001	0.005
P	0.005 - 1	0.002	0.005
C	0.01 – 100	0.001	0.01
S	0.01 – 10	0.002	0.01

Main characteristics of the implemented methods

Future work

We will bring the P measurement technique to its final development stage. This would allow us to further explore the applicability of the techniques to other cases (e.g. Ni-base alloys, stainless steels etc.), which will require to precisely define the scope of application as well as to quantify more exactly the acceptable ranges of concentrations of possibly interfering species and elements.

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Main references

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