Talanta 82 (2010) 1839–1844

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Low-level determination of silicon in steels by anodic stripping voltammetry on a hanging mercury drop electrode

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ARTICLE INFO

Article history:
Received 4 April 2010
Received in revised form 28 July 2010
Accepted 30 July 2010
Available online 7 August 2010

Keywords:
Silicon
Low-alloy steel
Differential pulse
Anodic stripping
Voltammetry
Hanging mercury drop electrode

ABSTRACT

The sensitive differential pulse anodic stripping voltammetry (DPASV) proposed originally by Ishiyama et al. (2001) has been revised and improved to allow the accurate measurement of silicon on a hanging mercury drop electrode (HMDE) instead of a glassy carbon electrode. We assessed the rate of formation of the partially reduced β-silicododecamolybdate and found that metallic mercury promotes the reaction in the presence of a large concentration of Fe^{3+}. The scope of the method has been broadened by carrying out the measurements in the presence of a constant amount of Fe^{3+}. The limit of detection (LOD) of the method described in the present paper is 100 μg Si g^{-1} of steel, with a relative precision ranging from 5% to 12%. It can be further enhanced to 700 ng Si g^{-1} of steel provided the weight of the sample, the dilution factors, the duration of the electrolysis and the ballast of iron are adequately revised. The tolerance to several interfering species has been examined, especially regarding Al^{3+}, Cr^{3+} and Cr VI species. The method was validated using four low-alloy ferritic steels certified by the National Institute of Standards and Technology (NIST). Its application to nickel base alloys as well as to less complicated matrixes is straightforward. It has also been successfully applied to the determination of free silicon into silicon carbide nano-powder.

1. Introduction

Silicon is being used as alloying element in various metallic matrixes like iron, steels or aluminium. Even at contents less than 0.1 wt.%, it can eventually modify the mechanical properties of the alloys and the machining capabilities as is particularly well known for aluminium. Therefore, its sensitive quantification in metallic alloys is essential. The sensitive determination of traces of silicon in metals, alloys and many other complicated matrixes is often plagued in the presence of other elements or species. For instance, ICP-MS measurements suffer from the isobaric interferences caused by $^{14}N_2{}^+$, $^{56}Fe^{2+}$, $^{12}C^{16}O^+$, $^{58}Ni^{2+}$, $^{14}N_2{}^1H^+$, $^{14}N^{15}N^+$, $^{13}C^{16}O^+$, $^{60}Ni^{2+}$, and $^{14}N^{16}O^+$ [2,3]. In the case of graphite furnace atomic absorption spectroscopy, the formation of refractory carbides worsens considerably the limit of detection (LOD) unless matrix modifiers are used [4]. ICP-AES, DCP-AES, IC, neutron activation as well as many other methods were found useful in particular cases but had also specific drawbacks. For these reasons, the spectrophotometric determination of the yellow silicododecamolybdate [5,6] as well as its enhanced version proposed originally by Mullin and Riley [7] remains very popular, although requiring also many precautions when dealing with complicated matrixes. Many elements can indeed form hetero poly-acids with molybdic acid [8–10]. Most of these complexes absorb light in the 300–450 nm range in their oxidised forms, and in the 700–900 nm range when partially reduced. Salt effects play also an essential role in such determinations, especially regarding the competition between the α- and β-silicododecamolybdate, which have different light absorption coefficients [11,12]. As a consequence, advanced but tedious kinetic measurements [13], chemical extractions [14] or separations [15] are often necessary to cope with interferences.

Although the electrochemical properties of hetero poly-acids were studied quite early [16–19], relatively few authors attempted to circumvent the above mentioned interferences by relying on the selectivity offered by electro-analytical methods [1,21–23]. Fogg and Osakwe [22] carried out the successful measurement of Si in low-alloy steels by differential pulse voltammetry (DPV) after the cathodic removal of interfering species and the masking of the excess of molybdate in a citrate buffer. They obtained a twin peak response at a mercury electrode. Using a glassy carbon electrode in citrate buffer solutions, Wang and Wang [23] observed a

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doi:10.1016/j.talanta.2010.07.079

Table 1
Reagents and solutions.

Reagent's ID	Description
1	Ammonium heptamolybdate 7.5 mM
2	Di-sodium tartrate 0.5 M in ammonia[a] 3.5 M
3	Silicon standard[a] ($SiCl_4$ in sodium hydroxide) $[Si]' = 20.3\ \mu g\ mL^{-1}$
4	Hydrogen peroxide 35 wt.%
5	Iron chloride $[Fe^{3+}]' = 10\ g\ L^{-1}$, $[HCl]' = 0.09$ M
6	Hydrochloric acid 6 M
7	Nitric acid 7 M
8	Acetone
9	Mercury
10	Potassium chloride

[a] Conditioned in a plastic container. Glass bottles should be avoided for this reagent.

Table 2
Electrochemical setup.

Experimental variable	This work	Ishiyama et al.
Deposition potential	−1.05 V	−1.1 V
Duration of the electrolysis step	80 s[a]	10 min
Equilibrium time	10 s	Not reported
Initial potential	−1.05 V	−1.1 V
Final potential	−0.525 V	−0.2 V
Scan rate	$10\ mV\ s^{-1}$	$50\ mV\ s^{-1}$
Pulse height	100 mV	100 mV
Pulse duration	40 ms	50 ms
Current range	10 μA full scale	Not reported

[a] The duration of the electrolysis may be increased up to 15 min if very low concentrations are to be measured.

multi-peak DPV response attributed to hetero poly-molybdosilicic acids. They reported interferences with Bi, but Fe, P, As, Cu, Mn, Co, Zn Al, Tl, Ni and Sn did not impair their measurements at 10 fold mass ratios with respect to Si. Using alternating current polarography (ACP), Barbosa and Tourinho [20] found that the simultaneous determination of the total silicon content is possible under well-chosen experimental conditions, regardless the repartition of silicon between the α- and β-silicododecamolybdate. Ishiyama et al. [1] reported the possible sensitive determination of silicon in steels by differential pulse anodic stripping voltammetry (DPASV) at a glassy carbon electrode, with no interference caused by phosphorus. Conversely, Chen [21] reported two well separated adsorptive responses on a static mercury drop electrode for the phospho-antimony hetero polymolybdate and the arseno-antimony hetero polymolybdate, respectively. Silicon did not interfere.

The main objective of this work was to improve the method proposed by Ishiyama et al. [1] in order to allow the accurate measurement of silicon at a hanging mercury drop electrode (HMDE) instead of a glassy carbon electrode, thereby avoiding the risk of cross contamination between successive measurements. A second objective was to assess the rate of formation of the silicododecamolybdate and to broaden the scope of the method, while minimising the duration of the analyses.

2. Experimental

2.1. Equipment

The working electrode was a PARC model 303 (EG&G), piloted by an Autolab model PGSTAT30 potentiostat (Metrohm, Ecochemie), using the GPES 4.9 software from Ecochemie. The surface area of the working electrode was $0.017\ cm^2$. The pHmeter was a Metrohm model 713. A MilliQ Direct Q 5 from Millipore was used as water purification unit. Chemicals and samples were accurately weighed on an analytical balance model AG204 from Mettler Toledo. All potentials were measured with respect to an Ag/AgCl, KCl 3 M reference electrode.

2.2. Chemical reagents and solutions

Analytical grade reagents and chemicals were used for all experiments. Table 1 defines the reagent's ID's referred to in the present paper. Stock solutions were stored in dark polyethylene (PE) bottles.

2.3. Metal sampling and sample preparation

2.3.1. Metal sampling

Metals were sampled according to the ASTM E1806-96 recommendations [24]. Addressing a range from 100 μg to 3 mg of silicon g^{-1} of alloy, we dissolved 100–1000 mg of metal.

2.3.2. Sample dissolution

Depending on the expected Si content, weigh accurately between 100 and 1000 mg of steel in a 100 mL PTFE beaker. Cover and stir gently. Add 2 mL of ultra pure water, next 1 mL of concentrated H_2O_2 (reagent 4). Add 10 mL of HCl 6 M (reagent 6). If needed, add regular aliquots (100 μL) of ultra pure H_2O_2 in order to sustain the formation of gas bubbles as long as the metal has not yet been completely dissolved. Add aliquots of HCl 6 M if needed for completing the dissolution of the metal. Heat-up gently, avoiding accelerating too much the decomposition of hydrogen peroxide. Once the dissolution is complete, let the mixture boil during a few minutes to eliminate hydrogen peroxide. Avoid going to dryness. Allow cooling down to room temperature. Transfer the liquid quantitatively into a clean 250 mL volumetric flask and dilute to the mark with ultra pure water. Mix thoroughly and transfer the sample liquor into a PE bottle.

2.4. Formation of the complex and electrochemical measurement

Transfer 40 mL of solution 2 into a clean 250 mL volumetric flask and store aside. In a clean 100 mL PTFE beaker, transfer 1.4 mL of HCl 6 M (solution 6), 2.8 mL of HNO_3 7 M (solution 7), 10 mL of iron chloride solution (solution 5), the sample containing Si, a PTFE coated magnetic rod, 170 mg Hg (reagent 9), 25 mL acetone (reagent 8) and 50 mL of ammonium molybdate (solution 1). Once these latter two reagents have been added, cover the beaker and stir the solution. After 30 min, transfer the liquid quantitatively (including Hg residues) into the flask containing solution 2. Dilute to 250 mL with ultrapure water and mix. The pH of this solution should be slightly above 10. Transfer portions of the liquid into PE cells, outgas the electrolyte by bubbling argon during 120 s and carry out the DPASV, according to the setup given in the second column of Table 2. The Si concentration in the electrolytic cell should lie between 10 and 150 ng mL^{-1}. To preserve all experimental conditions as prescribed in the present paper, the sample should not contain more than 10 mg Fe^{3+}, although 25 times more iron may be tolerated provided the setup is adapted. For calibration purposes, solution 3 can replace the sample. Table 3 summarises the various concentrations in the sample liquor, in the make up electrolyte as well as in the final electrolyte.

3. Results and discussion

3.1. Sample dissolution

A mixture of HCl and H_2O_2 is convenient for dissolving low carbon ferritic steels, provided hydrogen peroxide is boiled off after complete dissolution of the sample. However, we added nitric acid

Table 3
Analytical concentrations[a] of various species in the sample liquor, the complex make up electrolyte and the final electrolyte.

Solution[b]	Species	Units	This work	Ishiyama et al.
SL	Fe^{3+}	$mg\,mL^{-1}$	0.4–4	10
SL	H^+	$mol\,L^{-1}$	~0.24	~1.60
SL	Cl^-	$mol\,L^{-1}$	~0.24	~0.48
SL	NO_3^-	$mol\,L^{-1}$	0	~1.12
MUE	Fe^{3+}	$mg\,mL^{-1}$	1.1	2.5
MUE	H^+	$mol\,L^{-1}$	0.307	~0.4
MUE	Cl^-	$mol\,L^{-1}$	0.092	~0.12
MUE	NO_3^-	$mol\,L^{-1}$	0.215	0.28
MUE	Ammonium heptamolybdate	$mol\,L^{-1}$	0.0041	0.0038
MUE	Acetone	v:v ratio	0.274	0.25
MUE	Hg	mg	170	0
FE	Fe^{3+}	$mg\,mL^{-1}$	0.40[c]	1
FE[d]	H^+	$mol\,L^{-1}$	$\sim 10^{-10}$	10^{-10}
FE	Cl^-	$mol\,L^{-1}$	0.034	0.048
FE	NO_3^-	$mol\,L^{-1}$	0.078	0.112
FE	Ammonium heptamolybdate	$mol\,L^{-1}$	0.0015	0.0015
FE	Acetone	v:v ratio	0.1	0.1
FE	Sodium tartrate	$mol\,L^{-1}$	0.08	0.08

[a] Before any reaction occurred.
[b] SL: sample liquor; MUE: make up electrolyte; FE: final electrolyte.
[c] We added a controlled excess of Fe^{3+} to keep this figure constant.
[d] After neutralisation with solution 2.

at the stage of complex formation in order to preserve the possibility to switch back to *aqua regia* in more difficult cases. We limited the concentration of nitrates to 0.08 M in the final electrolyte to avoid any parasitic current possibly caused by nitrates during the measurement.

3.2. Make up of the silicododecamolybdate

Several attempts to measure Si under various conditions including the setup recommended by Ishiyama et al. [1] yielded inconsistent results on a mercury cathode. We suspected that the formation of the silicododecamolybdate was not quantitative and that mercury eventually influences the conversion, even at high pH. Therefore, we monitored the formation of the complex in function of time. We observed that the elements from the group IIb accelerate the formation of the silicododecamolybdate. The magnitude of the effect increases with the atomic mass (Zn < Cd < Hg). Attempts to accelerate the formation of the complex by using mercurous or mercuric ions failed. Therefore, it is not yet clear whether the metal acts as a catalyst or promotes the reaction by partially reducing the silicododecamolybdate. The latter reduction is clearly observed when using mercury. Since Cd and Zn dissolve easily at low pH, we focussed on Hg. Fig. 1 confirms that the quantitative formation of the silicododecamolybdate requires more than 2 h in the absence of mercury. Adding more than 170 mg of Hg yields no further increase of the reaction rate, the conversion being complete after 30 min. This is a major breakthrough with respect to the original work of Ishiyama et al. [1]. Indeed, these authors make up the complex during 30 min without using any promoting species. According to our results, the formation of the complex is not complete in these conditions (Fig. 1).

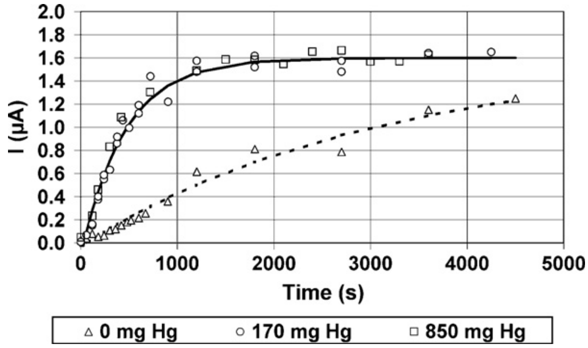

Fig. 1. Effect of mercury on the rate of formation of the silicododecamolybdate; total silicon concentration $[Si]' = 90\,ng\,mL^{-1}$.

3.3. Response on a mercury electrode

Ishiyama et al. [1] reported a multi-peak response at low pH when using either a carbon paste or glassy carbon or a hanging mercury drop electrode. They chose a glassy carbon electrode and carried out the stripping voltammetry measurement at pH 10, while masking iron with tartrate ions. They state that the glassy carbon can be used at least 20 times consecutively without describing any procedure for the cleaning of the electrode between successive measurements. To our opinion, solid electrodes require such cleaning procedure because the reduction products deposited during the electrolysis step are not necessarily completely re-oxidised during the voltammetric scan. Standing for a while at an anodic potential or even re-polishing the electrode are classical examples of such cleaning operations. In order to radically eliminate the possible influence of one measurement on the next ones, we decided to use a HMDE whose surface can be easily renewed by replacing the drop. This enhances considerably the work efficiency when carrying out series of measurements in routine. Using our experimental conditions, we observed also several peaks on the HMDE but the voltammograms obtained when scanning from the deposition potential up to −0.525 V allow the accurate measurement of silicon. The selective back oxidation of the molybdenum deposited on the electrode delivers a peak located between −0.67 and −0.79 V depending on the junction potential of the reference electrode bridge (Fig. 2). The exponentially decreasing baseline can be easily discriminated. One observes a second peak located around −0.64 V. The voltammograms reported by Ishiyama et al. do not show this peak, which does not impair the analytical determination of silicon. Using our setup, we assessed the effect of different variables as explained below.

3.3.1. Influence of the deposition potential

In contrast with the results reported in [1], the peak height observed on the mercury electrode keeps increasing when the deposition potential decreases down to −1.12 V and even lower.

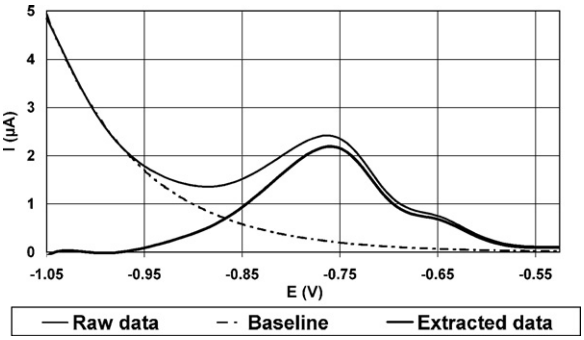

Fig. 2. Typical voltammograms observed on a hanging mercury drop electrode; $[\mathrm{Si}]' = 120\,\mathrm{ng\,mL^{-1}}$.

However, when the deposition potential is less than −1.2 V, several additional peaks appear on the voltammograms and the measurement becomes very difficult. As shown in Fig. 3, the peak height is constant with respect to the deposition potential only in a very narrow potential window (−1.02 to −1.05 V). Accounting for the progressive evolution of the junction potential that affects the reference electrode bridge, we fixed the deposition potential at −1.05 V and verified that the peak height remained linearly correlated to the Si concentration for any deposition potential chosen between −1.12 and −1 V. To cope with the overall slight drift of the reference electrode assembly, unknown standard samples were regularly measured to re-assess the slope of the calibration curve in function of time. Proceeding so allows carrying out over 50 measurements accurately without overhauling the reference electrode.

3.3.2. Influence of the pH at make up

Ishiyama et al. [1] report an increase of the peak height with increasing pH up to 0.5 at make up. They mention a decrease of the peak height when the pH at make up increases above 3. In contrast with these results, we observe a linear decrease of the peak height with pH increasing from 0.36 to 0.66. The influence of the acidity on the repartition of silicon between α- and β-silicododecamolybdates can eventually explain this behaviour but we have no clue regarding this assumption. Nevertheless, the acidity of the make up electrolyte should be carefully controlled to preserve the reproducibility of the results. When dissolving the steels as recommended in this paper, the residual acid present in the sample may be neglected. In any other case, the pH of the sample liquor should ideally be adjusted between 1 and 13 or the amount of acid added into the make up electrolyte should be adequately adapted.

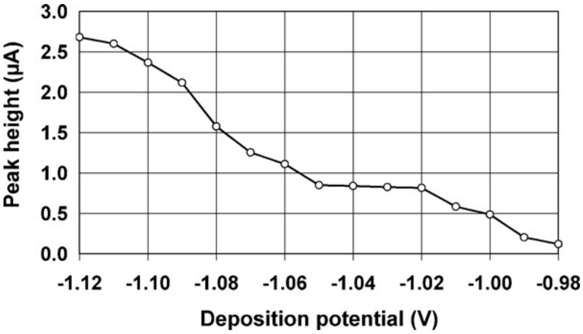

Fig. 3. Peak current (after subtraction of the baseline) in function of the deposition potential; $[\mathrm{Si}]' = 50\,\mathrm{ng\,mL^{-1}}$.

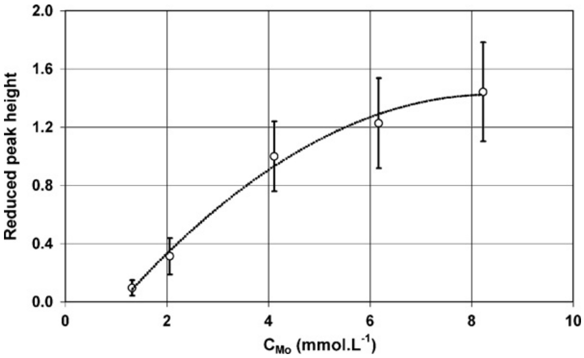

Fig. 4. Ratio of the peak height observed when using different molybdate concentrations C_{Mo} during complex make up to the peak height observed at $C_{\mathrm{Mo}} = 0.0041\,\mathrm{mol\,L^{-1}}$. Error bars correspond to the 90% confidence interval.

3.3.3. Influence of the molybdate concentration

Ishiyama et al. [1] observed that the peak height becomes independent of the molybdate concentration above $0.0038\,\mathrm{mol\,L^{-1}}$ in the make up electrolyte ($0.0015\,\mathrm{mol\,L^{-1}}$ in the final electrolyte). In contrast with these results, our measurements indicate that the response increases with increasing molybdate concentrations up to $0.008\,\mathrm{mol\,L^{-1}}$ in the make up electrolyte (Fig. 4). Moreover, the latter becomes cloudy for concentrations above $0.006\,\mathrm{mol\,L^{-1}}$. Therefore, we decided to limit the molybdate concentration to $0.0041\,\mathrm{mol\,L^{-1}}$ at make up.

3.3.4. Influence of acetone

Cetones are known to stabilise hetero poly-acids. Using our experimental conditions, the peak height is constant for a volume percentage of acetone in the make up electrolyte ranging from 20 to 50 vol.% (Fig. 5). These results are different from those reported by Ishiyama et al. [1] who observed a decrease of the response when using more than 25 vol.% of acetone at make up.

3.3.5. Influence of Fe^{3+}

Ferric ions have an adverse effect on the response. A linear decrease of the peak height is observed when the concentration of $\mathrm{Fe^{3+}}$ increases from 0.44 to $1.8\,\mathrm{mg\,mL^{-1}}$ in the make up electrolyte. In order to preserve the reproducibility, we decided to work at a constant concentration of iron ($C_{\mathrm{Fe}} = 1.1\,\mathrm{mg\,mL^{-1}}$) during the make up of the silicododecamolybdate. As long as the Si content in the steel remains above 0.01 wt.%, the iron present in the sample may be neglected with respect to the iron added to the make up electrolyte. However, if better detection limits are to be achieved, thereby requiring dissolving more metal, we recommend adapting the addition of iron in such a way that the total iron concentration

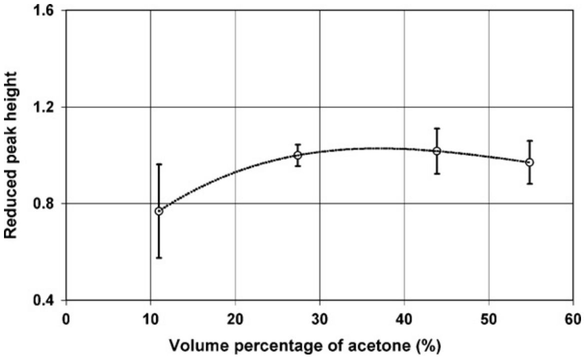

Fig. 5. Ratio of the peak height observed when using different volume percentage of acetone during complex make up to the peak height observed at a volume percentage equal to 27.4 vol.%. Error bars correspond to the 90% confidence interval.

Table 4
Statistics of the calibration curve and figures of merit.

Data	Value	Unit	Remarks
Slope	50.5	$\mathrm{ng\,mL^{-1}(\mu A)^{-1}}$	Reciprocal of the sensitivity
Intercept	6.1	$\mathrm{ng\,mL^{-1}}$	Statistically equal to 0
RCI[a] (slope)	5.3	$\mathrm{ng\,mL^{-1}(\mu A)^{-1}}$	90% confidence
RCI (intercept)	8.7	$\mathrm{ng\,mL^{-1}}$	90% confidence
Degrees of freedom	4		6 data points, 2 parameters
Percentage of variance explained	99	%	
Average deviation	4.4	$\mathrm{ng\,mL^{-1}}$	
Maximum deviation	6.1	$\mathrm{ng\,mL^{-1}}$	For $C = 0\ \mathrm{ng\,mL^{-1}}$
LOD (3 σ)	18	$\mathrm{ng\,mL^{-1}}$	
Relative precision	8.1	%	At 74.5 $\mathrm{ng\,mL^{-1}}$
Conc. Range	0 to 136	$\mathrm{ng\,mL^{-1}}$	

[a] Radius of confidence interval.

Table 5
Effect of possibly interfering species.

Species	Mass ratio tested	Result	Remarks
Al^{3+}	1000	No interference	
Al^{3+}	5000	Marked loss of sensitivity	At high mass ratios, Al^{3+} speeds up the formation of the complex
As (III)	100	No interference	As in concurrence with Si to possibly exhaust ammonium heptamolybdate during complex formation
Co^{2+}	30	No interference	
Cr^{3+}	100	No interference	Provided the electrochemical measurement is delayed by 2 h after the complex has been formed
Cr (VI)	50	Complete loss of Si response	Cr VI must be reduced to Cr^{3+}
Cu^{2+}	30	No interference	
Mn^{2+}	30	No interference	
Ni^{2+}	100	No interference	The method was validated with certified nickel base alloys
P (V)	1000	No interference	P in concurrence with Si to possibly exhaust ammonium heptamolybdate during complex formation
Sb (V)	30	No interference	
VO^{2+}	30	No interference	

remains constant in the make up electrolyte. Again, our results are different from those reported by Ishiyama et al. [1] who observed a constant response for C_{Fe} ranging from 0.250 to 1 $\mathrm{mg\,mL^{-1}}$ in the final electrolyte.

3.4. Figures of merit

The calibration data were fitted using a linear model. The corresponding statistics are given in Table 4. As mentioned in the experimental section, the recommended procedure is suitable for addressing up to 3 $\mathrm{mg\,Si\,g^{-1}}$ of alloy. In these conditions, the LOD is only 100 $\mathrm{\mu g\,Si\,g^{-1}}$ of alloy. However, we confirm that the LOD can be enhanced by a factor ~150 when increasing the surface area of the working electrode up to 0.07 $\mathrm{cm^2}$ and the duration of the deposition up to 15 min, while revising the dilution factors. These results are comparable to those reported in [1] (0.5 $\mathrm{\mu g\,g^{-1}}$ in the metal and 120 $\mathrm{pg\,g^{-1}}$ in the final electrolyte).

3.5. Interferences

Standard samples of silicon were measured in the presence of several possibly interfering species. For all measurements, the silicon concentration in the final electrolyte was 32 $\mathrm{ng\,mL^{-1}}$. The results given in Table 5 demonstrate that the method is suitable for the determination of Si in nickel base alloys. It can also be used to quantify Si in aluminium, provided the Si content is larger than 0.1 wt.%. Cr VI interferes strongly and has to be reduced to Cr^{3+} to allow the determination. Regarding this point, a mixture of HCl and H_2O_2 is particularly convenient for dissolving low carbon ferritic steels because it yields Cr^{3+} rather than Cr VI species. Even so, Cr^{3+} interferes unless the electrochemical measurement is delayed by 2 h after the formation of the complex. In contrast with the spectrophotometric approach, neither As nor P interfere provided enough ammonium heptamolybdate remains available for the make up of the silicododecamolybdate.

3.6. Validation using NIST certified standard steels

Four NIST certified ferritic steels were used for validating the method. Table 6 summarises the results, which are excellent.

3.7. Further applications

Although the method has been tuned for the characterisation of low-alloy steel samples, it can also be used to measure silicon in many other matrixes. Indeed, adding a controlled amount of iron to the sample before making up the complex allows addressing also iron free samples provided they do not contain other interfering species. Any kind of water (surface water, interstitial water, sea water, etc.) may virtually be considered after UV digestion. Soil extracts can also be addressed after a suitable pre-treatment. The excellent LOD and robustness of the method with respect to interfering species make it very tolerant to the dissolution process of samples containing more than 0.01 wt.% of silicon. As an exam-

Table 6
Certified composition (wt.%) of ASTM standard ferritic steels used for validation.

Steel ID	Certified content (wt.% Si)	Certified error (wt.% Si)	Measured value[a] (wt.% Si)	Radius of confidence interval (95%) (wt.% Si)	Nr. of replicates
30f	0.283	0.004	0.273.eps	0.056	4
291	0.23	0.007	0.237.eps	0.013	19
361	0.222	0.001	0.222.eps	0.027	4
362	0.39	0.01	0.41	0.078	3

[a] Figures reported with small fonts are not statistically significant.

ple, we used the revised method recently to detect and quantify small amounts of free Si and SiO_2 in silicon carbide nano-powder synthesized by a RF plasma torch. In this specific case, a selective dissolution was carried out using a mixture of NaOH, NaClO and H_2O_2. After filtration and dilution, the samples could be used without further treatment to form the complex in the presence of iron. This allowed tuning rapidly the stoichiometry of the final product by correctly adjusting the variables governing the plasma synthesis.

4. Conclusions

The sensitive DPASV of silicon reported by Ishiyama et al. [1] has been successfully adapted to carry out the measurement at a hanging mercury drop electrode instead of a glassy carbon electrode. Thereby, the risk of cross contaminations between successive measurements is completely eliminated.

A study of the rate of formation of silicododecamolybdate in the presence of a large amount of Fe^{3+} revealed that the reaction is complete within 30 min in the presence of metallic mercury.

We modified also the experimental procedures by adding a controlled amount of Fe^{3+} to the samples before making up the complex. This extended the scope of the revised method to various samples, without requiring specific adaptations, neither for the formation of the complex, nor for the electrochemical measurement.

The revised method tolerates the presence of many species that are known to interfere when quantifying the hetero poly-acid spectrophotometrically (a/o P, As, V). It can be applied to ferritic as well as to nickel base steels. It can also be applied to low-alloy aluminium provided the silicon content is at least 0.1 wt.%. However, the measurement is impaired when Cr VI is present at mass ratios ≥ 50. Even after reduction to Cr^{3+}, the correct determination of Si requires delaying the electrochemical measurement by at least 2 h after the complex has been formed.

The figures of merit reported in [1] were preserved. In particular, no separation step is needed, the measurement being fast and straightforward. We confirm that the LOD is 0.120 ng Si mL^{-1} in the electrolyte and 700 ng Si g^{-1} of alloy in the case of low-alloy ferritic steels. The precision of the method ranges from 5% to 12% relative to the mean measured values.

Acknowledgements

The authors wish to thank Dr. M. Scibetta (Head of MCA, SCK·CEN) and Prof. Dr. E. van Walle (General Manager, SCK·CEN) for their helpful support.

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