

Practical measurement of silicon in low alloy steels by differential pulse stripping voltammetry

A. Rahier, S. Lunardi, C. Triki

February, 2005

SCK•CEN
Boeretang 200
2400 Mol
Belgium

RMR

Practical measurement of silicon in low alloy steels by differential pulse stripping voltammetry

A. Rahier, S. Lunardi, C. Triki

February, 2005
Status: Unclassified
ISSN 1379-2407

SCK•CEN
Boeretang 200
2400 Mol
Belgium

RMR

Distribution list

Name	Institute	Number	Name	Institute	Number
A. Rahier	SCK•CEN	3	J.L. Puzzolante	SCK•CEN	1
S. Lundardi	SCK•CEN	1	P. Vanbree	SCK•CEN	1
C. Triki	SCK•CEN	1	L. Vandevelde	SCK•CEN	1
E. van Walle	SCK•CEN	1			
S. Van Dyck	SCK•CEN	1			
E. Lucon	SCK•CEN	1			
M. Scibetta	SCK•CEN	1			

		Date	Approval
Authors:	A. Rahier		
Verified by:	S. Lunardi		
Approved by:	E. van Walle		

© SCK•CEN
Belgian Nuclear Research Centre
Boeretang 200
2400 Mol
Belgium
Phone +32 14 33 21 11
Fax +32 14 31 50 21
<http://www.sckcen.be>

Contact:
Knowledge Centre
library@sckcen.be

RESTRICTED

All property rights and copyright are reserved. Any communication or reproduction of this document, and any communication or use of its content without explicit authorization is prohibited. Any infringement to this rule is illegal and entitles to claim damages from the infringer, without prejudice to any other right in case of granting a patent or registration in the field of intellectual property.

SCK•CEN, Studiecentrum voor Kernenergie/Centre d'Etude de l'Energie Nucléaire
Stichting van Openbaar Nut – Fondation d'Utilité Publique - Foundation of Public Utility
Registered Office: Avenue Herrmann Debroux 40 – B-1160 Brussel
Operational Office Boeretang 200, 2400 Mol, Belgium

Abstract

A sensitive differential pulse anodic stripping voltammetry has been adapted to allow the determination of Si in low-alloy steels using a hanging mercury drop electrode. The method has been qualified using certified ASTM standards and is now running in routine. The present report describes the experimental details, thereby allowing the reader to carry out the measurements precisely.

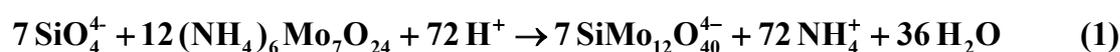
Keywords: silicon, low-alloy steel, differential pulse, anodic stripping, hanging mercury drop electrode

Table of content

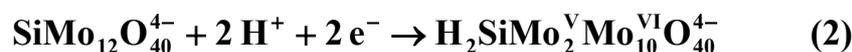
1	Introduction	1
2	Preliminary explanations: complement on the DPASV technique	2
3	Experimentals.....	5
3.1	Equipment, chemicals and solutions	5
3.1.1	Equipment	5
3.1.2	Chemicals.....	6
3.1.3	Solutions.....	7
3.1.3.1	Solution 1 (2 L)	7
3.1.3.2	Solution 2 (2 L)	7
3.1.3.3	Solution 3 (1 L)	8
3.1.3.4	Solution 4	8
3.1.3.5	Solution 5	8
3.1.3.6	Solution 6 (0.1 L)	8
3.1.3.7	Solution 7 (1 L)	9
3.1.3.8	Solution 8 (1 L)	9
3.2	Detailed procedure	9
3.2.1	Sampling.....	9
3.2.2	Dissolution of the metal	9
3.2.3	Formation of the complex	10
3.2.4	DPASV measurement	10
3.2.5	Data transfer	11
4	Practical tips	11
5	Data treatment	12
6	Example.....	13
7	Validation of the method.....	13
8	Conclusions	14
9	References	14

Introduction

In early 2004, the RMR department received a demand from an external client who asked us to carry out mechanical tests on activated low-alloyed steels. They asked also to characterize the local chemical composition of the samples. Silicon is one of the many elements that had to be analyzed. The quantitative determination of low concentrations of silicon in steels is not an easy task, although the basis of the most common analytical method for Si measurements in many different matrixes is known since more than 80 years. It relies on the (preferably quantitative) formation of the yellow β -silicododecamolybdate, starting from most soluble species containing silicon (meta⁻¹ and orthosilicates², silicon tetrachloride³, oligomers etc.). Reaction (1) illustrates the formation of the complex in the case of orthosilicates:



The complex concentration can be determined through the subsequent measurement of its absorbance around 420 nm. But as such, the method suffers from quite a lot of interferences (e.g. with P, As, and many other elements that can form similar complexes with the molybdates, all absorbing light around the same wavelength). Moreover, the detection limit of the original method ($\sim 500 \text{ ng.mL}^{-1}$ in the spectrophotometric cell) does not meet present requirements, while the kinetics of the complex formation is quite slow⁴. In 1962, focusing on P measurements, Murphy and Riley [2] could decrease the detection limit down to around 10 to 30 ng.mL^{-1} by partially reducing the yellow complexes by chemical means, yielding the so-called molybdenum blue complexes. In the case of Si, the reduction involves the following redox couple:



The blue complex can also be quantified through the measurement of its absorbance around 820 nm. But much interference with P (806 nm), As (880 nm), Sb, Ge etc. subsists since these elements yield also blue complexes with molybdates after partial reduction. As the sensitive measurement of Si along ICP-MS also suffers from interferences, especially when dealing with complicated matrixes like steels, we decided to develop a dedicated method. Through a fast survey of the most recent literature on the subject, we discovered an interesting article published by Ishiyama, Kobori and Tanaka [1]. These authors succeeded in determining 0.87 ppm of Si in high purity iron through differential pulse anodic stripping voltammetry (DPASV). They mention a detection limit as low as 0.5 ng.mL^{-1} in the polarographic cell and recommend 30 minutes for the formation of the complex⁵. They observed no disturbing effect in the presence of elements that usually interfere along the colorimetric approach. They used a glassy carbon (GC) electrode and reported some difficulties on a mercury electrode (a/o presence of several non reproducible peaks or a total absence of response).

¹ SiO_3^{2-}

² SiO_4^{4-}

³ SiCl_4

⁴ According to several sources, a reaction duration of at least three hours is needed to achieve a full conversion

⁵ When the reaction duration is less than three hours, the conversion might not be fully complete, thereby requiring a severe control of time to get reproducible results.

To our opinion, stripping measurements on glassy carbon electrodes require quite tedious intermediate treatments between successive measurements. Moreover, we have a ready-to-use mercury electrode associated with the necessary equipment to carry out sensitive DPASV in our laboratory. We wanted also to shorten the time required to achieve the full formation of the complex, with or without partial reduction. Therefore, we carried out research work on the quantification of Si along DPASV using a mercury electrode. Through systematic experimental work, we could define adequate operational conditions delivering two well-separated peaks, one of which being clearly associated to the partially reduced silicododecamolybdate. We could also decrease the duration of complex formation down to around 7 minutes by using a suitable catalyst. The latter converts also the yellow complex to molybdenum blue. We confirmed many results reported by Tanaka, a/o a very low detection limit that can indeed be pushed down to 0.5 ng.mL^{-1} in the polarographic cell. We further adapted the method to address higher Si contents in steels to match the expected ranges. In contrast with the glassy carbon electrode, the mercury electrode does not require intermediate cleaning operations when carrying out successive measurements: by simply discarding and replacing the drop after each measurement, we ensure that each determination occurs on a clean electro active surface.

Presently, the method runs in routine. In the future, we may possibly slightly amend the existing procedure to further facilitate the practical work in routine, but this does neither require any major revision nor involve additional research work. We consider that the method is mature.

The purpose of the present report is to describe the new analytical technique in full details. Thereby, we aim allowing the reader to carry out the measurements quite easily. In the short term, the routine measurements can be performed by the analytical services⁶, while we focus on the urgent development of other unresolved issues like P, S and C measurements in the same steels. Scientific aspects covering the enhancements we made for Si will be published later in an adequately chosen journal.

Preliminary explanations: complements on the DPASV technique

One full measurement requires carrying out the following four steps:

1. To dissolve the metal;
2. To make up the complex;
3. To record the polarogram;
4. To treat the data.

Steps 1, 2 and 4 require only common skills for analytical chemists. Therefore, preliminary scientific explanations will address step 3 exclusively.

Recording the polarogram consists in carrying out a **D**ifferential **P**ulse **A**nodic **S**tripping **V**oltammetry (DPASV) on the mercury electrode. Most operations are fully automated through the correct use of the electrochemical software controlling the potentiostat.

The DPASV is an anodic stripping technique. This means that after having installed the cell filled with the suitable electrolyte containing the unknown concentration of

⁶ The measurements may still be carried out in our laboratories, under our supervision. We keep ready to tackle any possible artifact that could be discovered later, e.g. when dealing with different matrixes.

silicododecamolybdate, and after having out gassed the solution by bubbling argon through it during at least 2 minutes, one carries out an electrolysis step by applying a suitably chosen cathodic potential difference between the working electrode and the built-in Ag/AgCl reference electrode. According to Tanaka and his co-workers, during this step, reaction (3) yields a black molybdenum oxide deposit on a glassy carbon electrode.



Several reasons let us think that exactly the same reaction occurs on mercury, although further reduction to an amalgam of Mo^0 is not excluded.

Note that the electrolysis has to be carried out in severely controlled conditions. Particularly, since the cathodic process runs under diffusion control, the hydrodynamics must be controlled. The reduction runs also at a well-defined potential with respect to the reference electrode, namely -1.05 V ⁷. Any junction potential across the sintered glass mounted on the reference electrode may cause a drift. Since the potential window wherein the method succeeds on mercury is narrow and since the reduction efficiency is extremely sensitive to the applied potential, care must be taken to replace the sintered glass as soon as poor results are observed (e.g. shifted peaks, or, in extreme cases, disappearance of the peak or appearance of multiple peaks⁸). Recent investigations revealed also that when a fresh sintered glass has been installed on the salt bridge, one should pay special attention to detect any initial drift of the potential⁹. The duration of the electrolysis is also essential: the longer it is, the more sensitive the method will be. Tanaka uses 10 minutes when addressing steels with low Si contents. We had to change this, because for now, we work with non-negligible amounts of Si in the steels (0.1 to 1 wt. %). ***We electrolyze during 80 s.*** Note that the electrolysis time may not be increased freely, because above an upper limit (depending on the complex concentration), the surface of the tiny mercury electrode may become saturated, thereby causing deviation from linearity on the calibration curve. Nonetheless, combining adequate dilutions and electrolysis potentials and durations, we confirm that it is perfectly possible to detect as low as 0.5 ng.mL^{-1} in the polarographic cell. That means also that slight adaptations of the method would indeed allow detecting fractions of ppm of Si in steels (i.e. $< 0.0001 \text{ wt. \%}$). There are two reasons why the method is so sensitive. First, the height of the peak (obtained as explained below) is proportional to the surface concentration of the Mo oxide produced during the electrolysis step (equation 3) on the surface of the tiny mercury electrode. Hence, the stripping technique offers a pre-concentration factor in relation with the ratio of the volume of electrolyte (several mL) to the volume of the mercury drop (a few mm^3). The second reason results from equation (3): it is Mo that reacts electrochemically, not Si. It is also Mo that will be re-oxidized during the next step (see below), thereby generating the peak used for quantification. But we have 10 Mo undergoing a 2-electrons reduction and 2 Mo undergoing a 1-electron reduction for 1 Si. Therefore, very small concentrations of Si (e.g. 30 ng.mL^{-1}) yields currents that are easily detectable (0.5 to $1 \mu\text{A}$), being generally far above the lowest current that can be measured by the sensitive I/E converter coupled to the potentiostat ($\sim 1 \text{ nA}$).

⁷ With recycled sintered glasses recently installed on the reference salt bridge, the voltage difference between the working electrode and the reference electrode should rather be equal to -1.00 V for best performances.

⁸ This was probably why Tanaka failed to find an acceptable setup on the mercury electrode.

⁹ A careful verification of the linearity of the calibration curve allows deciding whether the first measurements should be discarded or not. An eventual initial drift may not be immediate, but generally, the reference settles down quite fast to a potential value that remains sufficiently stable for carrying out a series of 25 to 50 measurements.

The next step of the DPASV measurement consists in back oxidizing part of the deposited molybdenum oxide¹⁰ during a scan towards positive potentials. For this, we use a Differential Pulse Voltammetry (DPV), similar to the one advised by Tanaka et al. Such technique has the advantage of both increasing the sensitivity with respect to the obsolete Heyrovsky method and differentiating the classical S-shaped waves, thereby yielding quasi-gaussian peaks. Without entering the details, we just mention that this technique is potentiostatic in nature, which means that the voltage difference between the working electrode and the reference electrode is imposed by the potentiostat during the experiment. Concurrently, and at well-synchronized sampling periods, the I/E converter measures the current flowing through the working electrode.

So, the effective measurement consists in back oxidizing the molybdenum oxide (or the molybdenum) by scanning towards positive potentials. This means that the device will slowly increase the potential of the working electrode with respect to the reference electrode. It does it essentially linearly with respect to time. But next to this, and at regular time intervals (to be chosen by the user), the potentiostat will superimpose positive potential pulses. The current is being sampled before the pulses and just at the end of the pulses. What is shown on the screen (and written on the hard disk) is the difference of these two currents for each pulse¹¹. So, a DPV is, in fact, a discrete technique (i.e. the current is sampled; it is not measured continuously).

Keeping this in mind, the user will have to define several variables describing the way the potentiostat should control the potential of the working electrode. Finding out the correct values for all these variables is beyond the scope of the present document: it all requires quite a lot of experience, because most variables have correlated effects on the result. Therefore, we will only give the values that were found through research work, thereby allowing the specific sensitive measurement of Si. These variables are as follows:

1. The so-called scan rate, generally expressed in $\text{mV}\cdot\text{s}^{-1}$: this is the slope of the basic linear relation between the working electrode potential and time. We work with $10 \text{ mV}\cdot\text{s}^{-1}$. Using the General Purpose Electrochemical Software (GPES) associated to our PGSTAT30 potentiostat, this value cannot be entered in one single field. With this instrument, the slope results from the ratio of the step potential to the interval time. See below for the definition of these variables;
2. The overall period of the current sampling: this is the interval time, fixed at 0.5 s . It is the regular time interval between two successive pulses;
3. The step potential: This is the potential increase (or decrease) observed after one interval time (the pulse having been reset!). In our case, this value is equal to 5 mV . Note that $(5 \text{ mV})/(0.5 \text{ s}) = 10 \text{ mV}\cdot\text{s}^{-1} = \text{scan rate}$;
4. The pulse height: It is fixed at 100 mV (which is quite high). The GPES calls it "the modulation amplitude" and expresses it in V;
5. The pulse duration: The GPES calls it "the modulation time", expressed in s. We fix it at 40 ms ;
6. The initial potential: It is the potential at which the device will start the scan. In our case, we fix it always at the same value as the deposition potential (normally, -1.05 V or -1.00 V);
7. The final potential: It is the potential at which the scan will be stopped. We fix it at -0.525 V .

¹⁰ This is the reason why we prefer mercury. Indeed, each measurement carried out on a glassy electrode would leave some molybdenum oxide on the electrode. This would impair the next measurement, unless an adequate treatment removes this residue quantitatively before proceeding to the next experiment.

¹¹ This is why this method is called "differential pulse voltammetry".

Besides these variables, we find also:

1. The purge time: **120 s**;
2. The deposition potential: **-1.05 V (-1.00 V when using a freshly installed sintered glass on the reference salt bridge)**;
3. The deposition time: **80s**;
4. Three conditioning potentials: all fixed at the same value than the deposition potential;
5. The duration of each conditioning: all fixed at **0 s**;
6. The equilibrium time: **10 s**;
7. The stirrer option: **ON**;
8. The "cell-off after measurement" option: **ON**;
9. The current range: it should be 10 μ A full scale. The corresponding option box (and only this one) should be checked and the green indicator should be bright;
10. The Potentiostat / Galvanostat option: it should read "Potentiostat";
11. The High Sense option: it should be turned off
12. The High Stability / High Speed option: it should read "High Stability";
13. The IR-Compensation: it should be turned off.

These experimental conditions were chosen to yield voltammograms that are similar to those obtained by Tanaka et al. on a GC electrode, while we are using a mercury electrode. They were also chosen to tackle the range of Si concentrations to be expected in low-alloyed steels. Depending on the practical circumstances (hydrodynamic conditions, junction potentials), these variables are likely to be adapted, but care must be taken that Si standards and steels of unknown composition can only be compared when measuring them all under exactly the same experimental conditions. The scan delivers a peak located between - 0.67 V and - 0.74 V on an exponentially decreasing baseline. We decided not to rely on the simple data treatment offered by the GPES. Data are exported to Excel and further treated using a VBA code specifically developed for this application (see further for illustrations).

Experimentals

Equipment, chemicals and solutions

Equipment

Common analytical glassware is used whenever the solutions to be measured do not stand for more than one hour in it. Stock solutions are also stored in glass bottles or volumetric flasks provided they are used within one week. For longer storage, it is advisable to use dark polyethylene bottles. Polytetrafluoroethylene (PTFE) beakers are used to dissolve the steels and to make-up the complex. PTFE or glass polarographic cells are used for the DPASV measurements, depending on the concentration levels (see further for explanations). Before being used, all flasks are washed thoroughly using the detergent listed in table 1. They are rinsed three times either with MilliQ water or with the adequate solution each time we change their content. Various regularly re-calibrated pipettes are used for volumetric operations (range: from 10 μ L up to 10 mL). All pipette tips are discarded after use. The polarographic stand is a PARC model 303 from EG&G, loaded with ultra pure mercury (see table 1). The potentiostat is an Autolab model PGSTAT30 from Ecochemie, connected to a PC along one dedicated USB port. We use the **General Purpose Electrochemical Software (GPES)** version 4.9 from Ecochemie as software.

The pHmeter is a Metrohm model 713 equipped with a Metrohm pH electrode (ref. 6.0238.000). A MilliQ Direct Q 5 from Millipore is used as water purification unit. Products are weighed on an analytical balance model AG204 from Mettler Toledo.

Chemicals

Table 1 gives a list of chemicals to be used for the measurements. Care must be taken not to use water from a different origin (e.g. LichroSolv certified water from the supply room is not convenient). All products that are used to make-up the electrolyte to be measured by DPASV must also be at least of analytical grade. All operations should be carried out in fume hoods.

Table 1: List of chemicals required for the measurement of Si in steels

Name	Formula /(molecular weight (g.mol ⁻¹))	Requirements	Origin
Ammonium heptamolybdate	(NH ₄) ₆ Mo ₇ O ₂₄ .4H ₂ O / (1235.86)	Analytical grade	VWR ref. MERC1.01180.111
Di-sodium tartrate	C ₄ H ₄ Na ₂ O ₆ .2H ₂ O / (230.08)	Analytical grade	VWR ref. MERC1.06663.1000
Silicon standard	1000 mg SiCl ₄ in NaOH 14 wt.% / (169.90)	Analytical grade	VWR ref. MERC1.09947.0001
Ammoniac 25 wt. %	NH ₃ / (17.03); d = 0.91	Analytical grade	SCK supply room
Hydrogen peroxide 35 wt. %	H ₂ O ₂ / (34.01); sp.gr. = 1.13	Analytical grade	SCK supply room
Iron chloride	FeCl ₃ .6H ₂ O / (270.30)	Analytical grade	Ref. Fluka 44944
Hydrochloric acid 37 wt. %	HCl / (36.46); sp.gr. = 1.19	Analytical grade	SCK supply room
Nitric acid 65 wt. %	HNO ₃ / (63.01); sp.gr. = 1.4	Analytical grade	SCK supply room
Aceton	C ₃ H ₆ O / (59.04); sp.gr. = 0.79	Analytical grade	SCK supply room
Water	H ₂ O / (18.02); sp.gr. = 1	MilliQ quality	Direct Q 5 unit from Millipore
Mercury	Hg / (200.59); sp.gr. = 13.6	> 99.999995 wt. %	Ref. Alfa (Johnson Matthey) #010634
pH buffer 1	n/a	pH = 4	JT Baker ref. 4795
pH buffer 2	n/a	pH = 7	VWR Titrisol ref. MERC1.09887
Detergent	n/a	n/a	Dreft 5-413149-007543

Solutions

Table 2 lists the solutions to be prepared.

Table 2: Solutions to be prepared for the determination of Si in steels

ID	Description	Advisable stock volume (L)
1	Ammonium molybdate ~ 7.5 mM acidified with HCl	2
2	Sodium tartrate ~ 0.5 M / NH ₃ ~ 3.5 M	2
3	Iron chloride (~ 10 mg Fe per mL) stabilized with HCl	1
4	Nitric acid ~ 7 M	2
5	Hydrochloric acid ~ 6 M	2
6	Silicon standard (20 µg Si per mL)	0.1
7	pH buffer 1 (pH = 4)	1
8	pH buffer 2 (pH = 7)	1

These solutions can be prepared as described below. Unless otherwise specified, only MilliQ water should be used, including for rinsing operations.

Solution 1 (2 L)

Prepare a 2 L volumetric flask. Clean it thoroughly and rinse it at least three times with MilliQ water. Weigh approximately 18.5379 g (NH₄)₆Mo₇O₂₄·4H₂O accurately in a small PE beaker. Note the exact weight W₁ (g) and add MilliQ water to wet the powder. Transfer the slurry quantitatively into the volumetric flask using a clean funnel and MilliQ water. Rinse the PE beaker and the funnel abundantly and transfer the rinsing water into the flask. Add about 1 L of MilliQ water to the flask, cork it and mix thoroughly until complete dissolution of the product. Open the flask, rinse the cork (transferring the rinsing water into the flask through the funnel), rinse the funnel and fill the flask up to 2 L. Cork back, write an identification mark (concentration and date) on the flask and store preferably in the dark. The concentration C_{M1} (mol.L⁻¹) to be written on the flask is calculated by:

$$C_{M1} = 4.04577 \times 10^{-4} \times W_1$$

Solution 2 (2 L)

Prepare a 2 L volumetric flask. Clean it thoroughly and rinse it at least three times with MilliQ water. Prepare a second volumetric flask (500 mL) the same way. Rinse the 500 mL flask with small portions of ammoniac 25 wt. %. Discard the rinsing solutions. Fill the volumetric flask with concentrated ammoniac 25 wt. % and adjust to volume. Cork the flask. Weigh approximately 230.08 g C₄H₄Na₂O₆·2H₂O accurately. Proceed in several steps if needed. Note the total weight W₂ (g). Wet the powder with MilliQ water and transfer it quantitatively into the 2 L flask, using a funnel. Use the 500 mL ammoniac solution to help the solid passing through the funnel. Transfer the remaining ammoniac from the 500 mL flask into the 2 L flask. Rinse the 500 mL flask three times with MilliQ water and transfer the rinsing water into the 2 L flask. Using a pipette whose volume is adjustable from 1 to 10 mL, add 25 mL of concentrated ammoniac solution (25 wt. %) to the 2 L flask. Rinse the funnel, transferring the rinsing water into the flask. Allow the solid to dissolve completely in the flask. Adjust to volume. Cork, write

an identification mark (concentrations and date) on the flask and store, preferably in the dark. The tartrate concentration C_{M2} (mol/L⁻¹) to be written on the flask is calculated by:

$$C_{M2} = 21.7316 \times 10^{-4} \times W2$$

Solution 3 (1 L)

Prepare a 1 L volumetric flask. Clean it thoroughly and rinse it at least three times with MilliQ water. Weigh approximately 48.4 g FeCl₃.6H₂O accurately in a small PE beaker. Note the exact weight W3 (g) and add MilliQ water to wet the powder. Transfer the slurry quantitatively into the volumetric flask using a clean funnel and MilliQ water. Rinse the PE beaker and the funnel abundantly and transfer the rinsing water into the flask. Allow complete dissolution of the product. Add 15 mL of HCl 6M (solution 5). Adjust to volume. Cork, write an identification mark (concentration and date) on the flask and store preferably in the dark. The iron concentration C_{M3} (mg.(mL)⁻¹) to be written on the flask is calculated by:

$$C_{M3} = 0.20661 \times W3$$

Solution 4

This solution is prepared by mixing equal volumes of MilliQ water and concentrated nitric acid (65 wt. %). Take care to always add the acid to the water. Allow cooling down. If necessary, proceed on a step-by-step basis and let tap water flow around the bottle to help cooling down. Rinse all materials thoroughly as usual.

Solution 5

This solution is prepared by mixing equal volumes of MilliQ water and concentrated hydrochloric acid (37 wt. %). Take care to always add the acid to the water. Allow cooling down. If necessary, proceed on a step-by-step basis and let tap water flow around the bottle to help cooling down. Rinse all materials thoroughly as usual.

Solution 6 (0.1 L)

This solution is made-up in two steps. The first operation consists in preparing 1 L of Si standard (mother solution), according to the manufacturer of the 1000 mg Si ampoule. In a second step, 2 mL of the mother solution are transferred into a clean 100 mL volumetric flask. To ensure the best precision, the 2 mL should best be weighed in a PE beaker. Note the weight W4 (g) and transfer quantitatively to the volumetric flask, using a funnel. Rinse both the PE beaker and the funnel abundantly with MilliQ water. Adjust to volume (still with MilliQ water) and transfer into a marked (concentration and date) PE bottle. As usual, all materials have to be cleaned and rinsed thoroughly. The mother solution may also be transferred into a marked PE bottle. The concentration C_{M4} (µg Si . (mL)⁻¹) is given by:

$$C_{M4} = 9.982 \times W4$$

Solution 7 (1 L)

This buffer should be made-up according to the instructions of the manufacturer.

Solution 8 (1 L)

This buffer should be made-up according to the instructions of the manufacturer.

Detailed procedure

Sampling

The amount of metal needed to carry out the measurement is highly dependent on the expected Si concentration in the steel. Presently, and although we could use less material when the Si content is above 0.1 wt. % in the steel, we work with at least 100 mg of metal and we recommend to use 250 mg. The shape of the sample has little importance, but we prefer chips sampled with a tungsten carbide drill (as recommended by ASTM E1806-96 (Standard Practice for Sampling Steel & Iron for Determination of Chemical Composition)). Generally, the volume of metal in one sample is approximately 15 - 35 mm³.

Dissolution of the metal

Using a clean 100 mL PTFE beaker¹², weigh approximately 100 – 250 mg of metal accurately. Note the exact weight W5 (g). Add a magnetic rod and put the beaker on the magnetic stirrer. Cover the beaker and allow the stirrer to rotate slowly. Using an adequate pipette, add gently 10 mL of HCl 6 M. Next, add 2 mL of H₂O₂ 35 wt. % **dropwise**. The reaction should run quite fast. Cover the beaker as soon as the hydrogen peroxide has been added. Cover it immediately if the reaction runs too fast, even if the hydrogen peroxide has not been fully added. The mixture will heat-up spontaneously and the metal should dissolve within 5 – 10 minutes or even less. Observe the liquid, taking care to recover any liquid from the cover each time it is removed. If black residues are visible, add 2 mL of H₂O₂ 35 wt. % again, still dropwise. Wait until all the residues are dissolved. If residues are still present, it could mean that the steel contains more than 0.5 wt. % of C in which case another dissolution technique should be applied (in development). When the solid is dissolved, add about 10 – 15 mL of MilliQ water, cover the beaker and heat-up gently until boiling. Let the solution boil for at least 3 minutes. Allow to cool down. Next, transfer the liquid quantitatively into a clean and well-rinsed 250 mL volumetric flask. Adjust to volume with MilliQ water and transfer immediately into a PE bottle. Write the following on the PE bottle:

- The identification of the metal (reference mnemonic);
- The weight of metal (W5);
- The volume (mL) of the volumetric flask used (normally 250);
- A reminder that H₂O₂ has been used for dissolving the metal.

¹² Beakers used for metal dissolution should not be used for other purposes.

Formation of the complex

Prepare a clean 250 mL volumetric flask. Transfer 40 mL of solution 2 in this flask. Cork and store aside for now. In a clean PTFE beaker, using adequate pipettes, transfer the following aliquots:

1. 1.4 mL of HCl 6 M (solution 5);
2. 2.8 mL of HNO₃ 7 M (solution 4);
3. 10 mL of iron chloride at 10 mg Fe per mL (solution 3);
4. The solution containing Si; we have three cases:
 - a. We make a blank in which case no Si is added;
 - b. We analyze a sample of unknown composition; typically, 2 mL of the dissolved metal solution are recommended, but if it appears that the Si content is very low, the experiment should be repeated with more liquid (up to 7 mL maximum);
 - c. We analyze a standard: in this case, from 200 to 3000 μL of the Si standard (solution 6) may be added. The volume depends on the targeted calibration point. Remind that according to the present recommendations, the Si concentration in the polarographic cell should ideally lie between 20 and 150 $\text{ng}\cdot\text{mL}^{-1}$, while we will dilute the complex into 250 mL (see below).
5. A magnetic rod;
6. 20 μL Hg;
7. 25 mL acetone and 50 mL of ammonium molybdate (solution 1). These reagents should ideally be added together. Once they are added, the beaker **must** be covered and placed on the magnetic stirrer. **A timer has to be started and one should proceed to the next step after 15 minutes.**

Note that series of beakers may be prepared. In this case, prepare them up to step 5 (included). At this stage, the pH should be around 0.7 (to be checked regularly). Steps 6 and 7 should only be carried out to initiate the complex formation.

Once step 7 is completed, the stirrer should be stopped and the liquid¹³ should be transferred quantitatively into the flask containing the tartrate. The beaker, the cover and the funnel have to be rinsed adequately with MilliQ water. Adjust to volume, cork and mix thoroughly. The pH of this solution should be around 10 (to be checked regularly). Transfer portions of the liquid into PE beakers and proceed to DPASV, preferably within 10 – 20 minutes. This solution will be referred to as "the electrolyte" in the next steps.

DPASV measurement

We consider that the potentiostat is on and that the GPES software is running. Under "Methods", select "Voltammetry", next "Differential pulse". Refer to point 2 to prepare the set-up. Turn the cell off using the button located on the front panel of the potentiostat and check the connections of each electrode. Ensure that the interface driving the Model 303 is on (the red light should be on). Ensure that the argon cylinder is open. Rinse and dry partially the electrodes using an absorbing paper (make use of capillarity; avoid touching the electrodes). Using adequate pipettes, transfer 15 mL of the electrolyte to the polarographic cell. Proceed to the measurement by clicking on the start button. The system should deliver an answer similar to the one shown of figure 1.

¹³ Including Hg residues.

Each sample should be recorded at least four times, replacing the electrolyte into the measurement cell before each scanning. The four measurements should be loaded as overlays to check for reproducibility. If the spreading appears to be high (visual appreciation), carry out at least four additional scans. It is also advisable to carry out at least two experiments involving separate complex formations. If the dispersion due to sampling is of any interest, separate metallic samples should be dissolved and submitted to the procedure.

Data transfer

Once a measurement has been taken, save it on the hard disk along "File", 'Save data as...". Choose a filename that allows to quickly identifying to which measurement the files correspond. Ideally, the filename should contain the following information:

1. A sample identification: either the mnemonic used to name the steel, or the type of standard that has been measured (volume and concentration of the Si standard);
2. The volume of the aliquot taken from the dissolved sample (if dealing with a steel);
3. The potential at which the deposition was carried out;
4. The eventual use of the stirrer ("mix" or "nomix");
5. A number associated to the replicate;
6. The purge and deposition times;
7. The date.

Use well structured directories to store the files.

When saving the results, the computer generates ***three files***, using the given filename and defining extensions as explained below:

- A data file containing the successively measured currents and the corresponding potentials (extension .oew);
- A set-up file containing detailed information of the setup under which the measurement was carried out (extension .iew);
- An auxiliary configuration file describing the way the curve was displayed by the GPES (extension .iei).

Just keep all these files under the same directory and take care to ***always transfer all of them for further data treatment***. Transfer of the data should be done along an USB stick¹⁴. See point 5 for some details about the data treatment.

Practical tips

- The sensitivity of the answer depends strongly on the deposition potential. But the electrolytes are quite viscous and their composition is very different from the electrolyte used in the salt bridge of the reference electrode (KCl 3 M). Therefore, as series of measurements progress, the sintered glass separating the reference electrolyte from the

¹⁴ Our policy is not to connect laboratory computers to the network to preserve the systems from any malfunction resulting either from other applications that could be installed or from Internet surfing. Each laboratory computer is dedicated to drive one single and specific instrument.

measured electrolyte becomes slightly clogged. The corresponding junction potential increases with time and the sensitivity is being affected. The symptoms of such drift are:

- A shift of the peak towards apparently more negative values. The position of the peak should not be below -0.75 V vs. the reference electrode;
- A clear decrease of the sensitivity.
- To cope with the above effect, it is necessary to alternate measurements of unknown samples with calibration points. Ideally, the measured sample should deliver a peak whose height is located between the standards measured before and after the sample;
- When using a freshly installed sintered glass on the reference salt bridge, some initial drift may affect the potential of the reference electrode. Care must always be taken to keep an eye on the linearity of the calibration curve prior accepting the results;
- When the PARC Model 303 has not been used during several hours, the contact with the mercury drop along the capillary and the valve body is generally interrupted. To restore the contact, switch the Model 303 on DME (Dropping Mercury Electrode) for at least 10 s. Next, switch it back to HMDE, install and discard at least 5 drops and check for contact;
- Erratic measurements accompanied with a warning saying that the measurement can be repeated using a lower current range are generally due to a disconnected cell (check the right button on the potentiostat: the yellow light should be on) or to a bad contact along the mercury column (see previous point);
- In the conditions described by the present procedure, the detection limit is around 5 ng Si per mL in the polarographic cell. Using 250 mg of metallic sample with a 2 mL aliquot of the solution resulting from the metal dissolution, this corresponds to 0.0625 wt. % Si in the metal. Adapting the volumes and the weight of the sample allows detecting much lower Si contents in the metal. The calibration remains linear up to at least 150 ng Si per mL in the electrolyte. This allows addressing up to 1.875 wt. % in the sample without modifying the procedure;
- The dispersion of the results ranges from 7 to 12 %. This is a typical figure associated to low-level DPASV measurements¹⁵;
- Even much higher sensitivities may be achieved when using forced convection during the deposition process. However, in the present status of the method, the dispersion suffers from insufficiently reproducible hydrodynamic conditions (20 % dispersion and above in the worst cases).

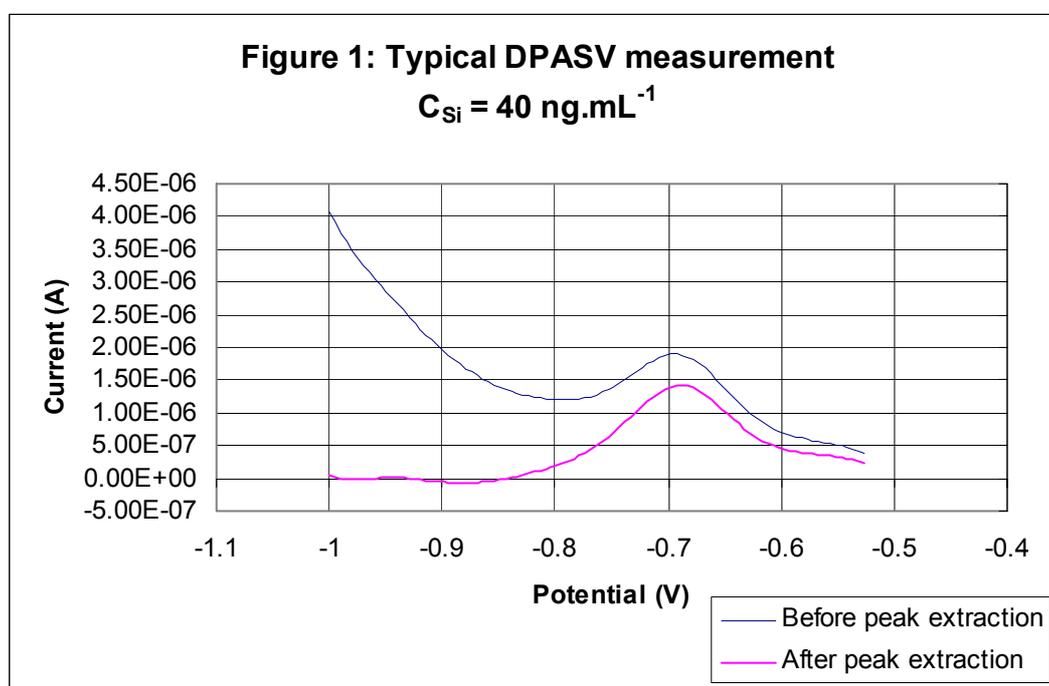
Data treatment

The files generated by the GPES are treated numerically under Excel, using a code specifically designed to discriminate the peak from the baseline. The code uses curve fitting and smoothing (method of Savitzky and Golay). It requires registering a homemade OCX on the local machine. After extraction of the peak, the maximum current is plotted versus the concentration in the electrolyte to yield calibration data.

¹⁵ The reproducibility of the electrode area ranges from 3 to 5 %.

Example

Figure 1 illustrates a typical polarographic answer obtained using an electrolyte containing a calibrated amount of Si (40 ng.mL^{-1}). The original curve is the one showing a general trend of the current that decreases exponentially with increasing potentials. The second curve illustrates the peak after numerical extraction. Note the presence of a second peak after the main one. This small peak has not been attributed clearly, but it is always present, even when using Si standards. This let us think that it corresponds also to the back oxidation of the deposit formed during the electrolysis. Extending the scan to more positive potentials reveals another peak¹⁶ that develops slowly with time. This peak appears not to be related to the Si content. Without certitude, it could be due to the excess of reagent used for the formation of the silicododecamolybdate.



Validation of the method

Measuring ASTM steels with certified Si contents has validated the method. Table 3 summarizes the qualification results. The data corresponding to ASTM 363 show also that the new dissolution technique designed to avoid nitrate ions is not efficient when the C content exceeds 0.5 wt. %. For such high C content, another dissolution technique is currently being examined.

¹⁶ Not shown on figure 1.

Table 3: Qualification measurements¹⁷

ASTM steel ident.	Certificate		Measurements		
	Mean wt. %	Est. Error	Mean wt. %	Est. Error	Nr. replicates
30f	0.283	0.004	0.273	0.056	4
291	0.23	0.007	0.237	0.013	19
361	0.222	0.001	0.222	0.027	4
362	0.39	0.01	0.410	0.078	3
363	0.74	0.01	0.168/0.453	-----	8/6

Numerous additional measurements were also successful. They were carried out using either non-certified alloys whose Si content has been abundantly reported in the literature, or alloys of unknown composition for which SCK clients knew about the range of Si concentration(s) to be expected. Furthermore, the method was also successfully applied to nickel base alloys.

Conclusions

The quantitative measurement of Si in low-alloy iron steels can be carried out by a sensitive differential pulse anodic stripping voltammetry. The method was originally developed in Japan but we adapted it to our specific requirements, taking available equipment and expertise into account. After having qualified the method by carrying out successful measurements on certified standards, we can now run the experiments in routine operation.

References

1. Ishiyama T., Kobori T., Tanaka T., "Sensitive stripping voltammetry of silicon (IV) and its application to steel analysis", *Bunseki Kagaku*, 60, 8, pp. 531-536 (2001)
2. Murphy J. and Riley J.P., "A modified single solution method for the determination of phosphate in natural water", *Analytica Chimica Acta*, 27, 31-36, 1962.

¹⁷ The measured figures are given with one digit beyond the dispersion in order to give a better idea of the accuracy.