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DETERMINATION OF PHOSPHOROUS, SUPLHUR, AND SILICON CONTENT OF LOW-ALLOYED AND UNALLOYED STEEL BY ICP-AES AFTER A UNIFIED WET CHEMICAL SAMPLE PREPARATION PROCEDURE

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Phosphorous, sulphur, and silicon have a great effect on the mechanical characteristics and metallurgical properties of steel. Therefore, it always has been important to know their concentration either in the unalloyed or in the alloyed metal. Using only wet chemical methods their analysis takes much time and labour. The modern instrumental methods make it possible to carry out their determination in a very short time, but the special equipment necessary for that is rather expensive and can be operated efficiently only if there are a lot of samples to be analysed. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) needs liquid samples, so solid samples must be dissolved prior the analysis. Using this technique, however, one can analyze almost any substance that can be taken into solution provided that there is a suitable sample preparation procedure at the user's disposal. In this paper, a wet chemical sample preparation procedure is presented, which seems to be suitable for the determination of these important constituents of the steel.

Keywords: wet chemical sample preparation procedure, ICP-AES analysis, determination of P, S and Si content of steel

Introduction

Phosphorous, sulphur, and silicon are rather important constituents of steel, because they have a strong influence on its properties. As a consequence of that fact, it has always been important to know their concentration in the alloy. Before the advent of the powerful instrumental methods, their analysis was performed by gravimetric and volumetric wet analytical procedures, which took a lot of time and labour [1, 2].

Because of the development of instrumental analysis and that of the equipments, new instrumental methods based upon mostly spectrochemistry have been developed, which can produce almost complete elementary analysis of metals and metal alloys. As they need solid samples and as a consequence of that, the sample preparation is simple and fast: the analytical results are at the disposal of the user in a very short time. Their only disadvantage is the need of special instrument, i. e. usually an optical emission spectrometer using spark or arc excitation, which is normally specially designed for the analysis of a given group of metals or alloys. Therefore, their economic use demands large load of the same or similar type of samples.

The laboratories meeting general analytical demands cannot operate such special equipment in an economic way because of the insufficient number of samples to be analyzed. Instead of the methods requiring solid samples, they prefer the application of analytical techniques that need liquid-type samples. Solid samples need to be taken into dissolution prior the analysis. Although the methods based on dissolution of the solid samples may have several drawbacks – such as much time may be necessary to dissolve the sample, sample losses may occur, or the sample may be contaminated either from the dishware or from the chemicals, etc. –, the methods using wet chemical sample preparation have some definite advantages: almost any kind of sample can be used and normally there is no need to have many special certified reference materials to perform the calibration. If a flexible emission spectrometric instrument, such as an inductively coupled plasma (ICP) spectrometer is used for the analysis, by the use of wet sample preparation procedures the overhelming part of elementary analytical tasks can be performed. Therefore, this might be an ideal solution for laboratories performing general analytical tasks.

In case of the inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis of steel, the analytical parameters are well-known. For most of the components, the spectral lines, where no or only very little spectral interferences can be observed, are at the user's disposal and by performing the calibration with the help of the so-called matrix-matching technique most of the chemical interferences can be eliminated.

Regarding the sample preparation methods, most procedures suggested for sample preparation dissolve the steel sample in hydrochloric acid [3]. This acid is able to dissolve almost all kinds of steel and most metallic constituents will be dissolved and will remain in solution, but regarding P, S, and Si its use has some drawbacks. In the course of the dissolution in hydrochloride acid, H_2S and PH_3 may form. These components are volatile, which may lead to S and P losses. Silicon may form SiO_2 during the process and it may be partially dehydrated, especially when the solution is heated up to its boiling point. The dehydrated silicon-oxide will be no longer soluble in the solution, which also causes analyte losses.

Using nitric acid instead of hydrochloride acid [4], S will form SO_2, which produces H_2SO_3 with water, while P will form H_3PO_3. Si will form SiO_2, but it will not tend to deposit in the nitric acid solution.

Based upon this dissolution procedure, we developed a unified sample preparation method, which is suitable for the determination of P, S, and Si. In the following, the details of the sample preparation procedure, the conditions of the ICP analysis, and the analytical results with some performance characteristics are reported.

Experimental

The sample preparation procedure

Because of the above-written properties nitric acid was chosen as dissolving agent. So that many types of steel could be dissolved, dilute (1:3) nitric acid was used. According to our experiences, it is able to dissolve unalloyed steel and most of the low-alloyed steels.

After the dissolution, 2 m/m% $KMnO_4$ solution was added to the liquid to oxidize P. The excess of the oxidizing agent was decomposed by adding 2 m/m% $NaNO_2$ solution. When the clean solution cooled down, it was taken into a plastic volumetric flask and 0.5 cm^3 HF was added to the sample. The HF will dissolve SiO_2, no matter whether it is in solution or it is deposited. Care should be taken that no free HF should remain in the solution, because it may damage the torch and the spray chamber if they are made of silicon-based material. Therefore, 5 cm^3 4 m/m% H_3BO_3 is added to the solution.

The ICP instrument

In the course of the analysis, the Varian-make 720 ES instrument, an axially-viewed simultaneous multielement ICP spectrometer was used. This instrument has a specially designed “Echelle” optical system, equipped with a two-dimensional CCD detector. The optical system is able to process the wavelength-range of 160-780 nm. It has a free-running high frequency generator operating at 40 MHz. Its power applied to the torch can be adjusted from 800 W up to 1500 W in 50 W steps by the controlling software. Because of the properties of the optical system, it is possible to choose several lines for the elements to be measured, which can be especially advantageous in the case of unexpected spectral interferences (e. g., when samples with unknown composition are to be analyzed).

The measuring conditions

The spectral lines chosen for analysis can be seen in *Table 1*. In the course of the measurement, 1050 W high-frequency power was applied to the torch. The integration time was 8 s and the intensity values were obtained by averaging three consequent readings for each sample. As for the sample introduction, K-type glass-made pneumatic nebulizer and cyclone-type spray chamber were used.

Table 1: The measured spectral lines

P	177.43 nm	178.22 nm	213.62 nm
S	180.67 nm	181.97 nm	-
Si	212.41 nm	251.61 nm	288.16 nm

The samples for calibration and obtaining the performance characteristics

To perform calibration of the analytical programme and to obtain some performance characteristics, certified reference material samples (CRMs) were used, which were prepared using the above-written procedure. So that one could judge how well the method, especially the sample preparation procedure meets the requirements, several certified reference material samples were chosen so that different types of low-alloyed steel could be represented among the samples. The chemical compositions of the selected CRMs are presented in *Table 2*.

Table 2: Chemical compositions of the CRMs chosen for calibration and determination of some performance characteristics*

Identifier	C	S	Si	P	Mn
ASNW Nr 177	0.036	0.003	0.223	0.014	0.18
ASMW Nr59/2	0.40	0.033	1.61	0.039	0.65
ASMW Nr 162	0.37	0.020	1.40	0.031	1.27
ASMW Nr 174	0.43	0.024	0.39	0.032	1.78
ASMW Nr 103	0.176	0.010	0.50	0.013	0.46
ASMW Nr 159	0.127	0.042	0.30	0.086	0.521
ASMW Nr98/1	0.16	0.016	0.32	0.011	0.40
Identifier	Cr	Ni	Cu	Mo	V
ASMW Nr 177	0.117	0.167	0.058	0.068	0.061
ASMW Nr59/2	-	-	0.14	-	-
ASMW Nr 162	-	-	-	-	-
ASMW Nr 174	0.143	-	-	-	0.008
ASMW Nr 103	1.29	0.11	-	1.08	0.300
ASMW Nr 159	0.76	0.13	0.36	-	0.047
ASMW Nr98/1	1.36	3.53	-	-	-

*all the data in *Table 2* are given in m/m%

Results

In the course of the experiments and measurements, the determination of the detection limits representing the detection power was carried out, which was followed by obtaining the calibration curves. Following that, the repeatability of the method was tested using reference materials.

Determination of the detection limits

The determination was carried out using the CRM Nr 174. 0.4 g sample was taken into solution with the help of the above-written sample preparation procedure. The volume of the solution was made up to 0.1 dm^3, so the resulting concentration of P, S and Si were 1.28 mg/dm^3, 0.96 mg/dm^3 and 15.6 mg/dm^3, respectively. The details are in *Table 3*.

Table 3: The detection limits obtained for the three elements with the help of the developed method

Element	Wavelength	DL, mg/dm^3	DL, m/m%*
P	177.43 nm	0.024	0.0006
	178.22 nm	0.034	0.0008
	213.62 nm	0.025	0.0006
S	180.67 nm	0.011	0.0003
	181.97 nm	0.018	0.0005
Si	212.41 nm	0.059	0.0015
	251.61 nm	0.039	0.0010
	288.16 nm	0.041	0.0010

*sample mass is 0.4 g; volume of the solution is 0.1 dm3

Calibration

Calibration is a key question of each analytical method, as it will ensure the traceability of the measurements. In the case of a method that requires liquid samples – and the results are referred to a solid state sample –, calibration can be carried out either by using calibration solution series composed of mono- or multi-element certified reference material solutions or with the help of solid CRMs prepared in the same way as the samples. The first way is easier as it will not need special solid steel CRMs, but the effect of sample preparation procedure might not be taken into account during calibration and it also may be that the chemical form of some elements present in the sample is not the same in the calibration solutions. So that this problem could be avoided, the calibration was carried out by using solid CRM samples prepared in the same way as the samples were. The list of the calibration standards can be seen in *Table 2*. Looking at *Table 3*, it can be seen that there is hardly any difference concerning the detection power on all lines chosen, therefore, it seemed to be interesting whether there would be any difference regarding the calibration. The calibration curves are presented in *Figure 1*, *Figure 2*, and *Figure 3*.

The most important characteristics of the calibration curves can be found in *Table 4*.

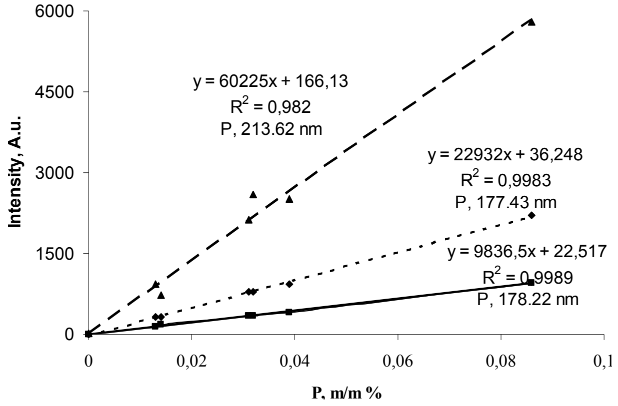

Figure 1: Calibration curves obtained on P lines

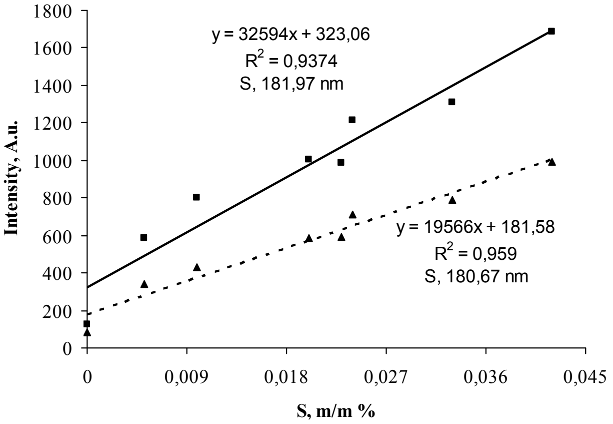

Figure 2: Calibration curves obtained on S lines

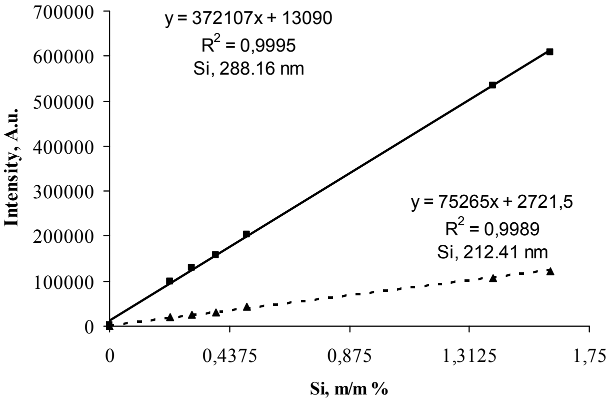

Figure 3: Calibration curves obtained on 2 Si lines

Determination of the repeatability

In order to determine the repeatability of the method, 2 CRMs, which were not used in the course of calibration, were chosen and 5 parallel samples from each standard were prepared using the above-written sample preparation procedure.

Table 4: Important parameters of the calibration curves

Element	Wavelength	R (Corr. Coeff.)	SD_{cal}
P	177.43 nm	0.99915	0.00127
	178.22 nm	0.99945	0.00102
	213.62 nm	0.99096	0.00423
S	180.67 nm	0,97929	0.00242
	181.97 nm	0,96819	0.00248
Si	212.41 nm	0.99942	0.0210
	251.61 nm	0.99910	0.0172
	288.16 nm	0.99975	0.0134

The chemical composition of these samples concerning the 5 base elements is presented in *Table 5*. For both standard samples the averages and the standard deviations (SD), as well as the relative standard deviations (RSD%) were calculated from the results obtained for the 5 parallel samples and they can be found in *Table 6*.

Table 5: The chemical composition concerning the 5 base elements of the standard samples used for the determination of the repeatability*

Identifier	C	S	Si	P	Mn
A 12	0.04	0.065	1.20	0.019	0.31
A 17	0.78	0.023	0.37	0.038	1.79

*all the data in *Table 5* are given in m/m%

Table 6 : The repeatability determined from 5 parallel measurements

Sample	Element, line	$C_{average}$ m/m%	RSD%
A 12	P, 177.43 nm	0.0182	0.83
	P, 178.22 nm	0.0171	2.05
	P, 213.62 nm	0.0176	1.14
	S, 180.67 nm	0.0661	6.97
	S, 181.97 nm	0.0629	6.47
	Si, 212.41 nm	1.18	1.53
	Si, 251.61 nm	1.18	1.55
	Si, 288.16 nm	1.17	1.60
A 17	P, 177.43 nm	0.0415	2.01
	P, 178.22 nm	0.0407	1.89
	P, 213.62 nm	0.0411	2.77
	S, 180.67 nm	0.0262	2.59
	S, 181,97 nm	0.0257	2.25
	Si, 212.41 nm	0.361	8.71
	Si, 251.61 nm	0.371	9.01
	Si, 288.16 nm	0.368	8.83

Discussion of the results

Steel is usually regarded as a difficult matrix from the viewpoint of chemical analysis. This is because this material often contains elements with different chemical properties and behaviour. As for the atom-spectroscopy, the main constituent of steel, i. e. iron, is very rich in spectral lines, therefore, the possible spectral interferences always have to be encountered in the course of method development. If wet chemical sample preparation has to be applied, further difficulties may be encountered because it is difficult to develop a sample preparation procedure (that is suitable for all constituents) due to the large differences in the properties of the components. In the case of phosphorous, sulphur, and silicon, the main difficulty is that the usual method, i. e. dissolution of the sample in hydrochloric acid, cannot be used because volatile compounds may form, which can cause analyte losses. On the other hand, silicon is partially dehydrated in hydrochloric acid, therefore, again, analyte losses may occur. Using nitric acid as a dissolving agent, care must be taken to avoid metal passivity. That is why dilute nitric acid is used in our method. It is also very important that the elements to be determined should be in proper oxidation state. The role of $KMnO_4$ is to meet this requirement.

From the chemical composition data, it is obvious that this procedure is suitable for most unalloyed and low-alloyed steels. For highly-alloyed steels, e.g. stainless steels, it is not suitable as the occurrence of the passive state cannot be avoided because of the high chromium content.

Although there is a substantial dilution because of the dissolution, the detection power reached is suitable for the determination of all the three elements, even at low (0.005%) phosphorous and sulphur concentration.

The calibration resulted in linear curves for all elements, and the standard deviation of the curves is rather low, so they can be used down to 0.005% for P and S and about 0.05% for Si. The only exception may be the 213.62 nm phosphorous line, as its standard deviation reaches 0.004%, therefore, its lower limit of the analytical working range is 0.01%.

The repeatability values were determined by preparing and measuring 5 standard samples. The obtained data prove that the method is suitable to determine these three elements in a wide concentration range. Comparing the repeatability values of S to those obtained by using combustion methods with non-dispersive IR detection, it can be stated that both methods have approximately the same repeatability.

Finally, one may ask when this method is worth using by the analyst. Regarding the fact that much time is necessary for the wet chemical preparation, this method cannot compete with fast methods, which must be used when there is only little time at the analyst's disposal. On the other hand, if the analysis time is not of key-importance, this method may be applied, especially when the special equipment necessary for the spark or arc optical emission spectrometry or x-ray fluorescence is not available.

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