UDK 669.15'777'4:543.428.2
Izvirni znanstveni članek

ISSN 1580-2949
MTAEC 9, 36(6)325(2002)

A SIMULTANEOUS DETERMINATION OF THE LEVELS OF LEAD, SELENIUM AND TELLURIUM IN STEEL USING ICP-AES

SIMULTANO DOLOČEVANJE Pb, Se IN Te V JEKLU Z ICP-AES

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Prejem rokopisa - received: 2002-11-12; sprejem za objavo - accepted for publication: 2002-12-05

We have developed a useful procedure for the simultaneous determination of Te and Pb in low-alloy steels in the 5.0-100 $\mu g g^{-1}$ range using ICP-AES after the chemical separation of the iron and the pre-concentration of Te and Pb by a batch process. The procedure is based on the liquid-liquid extraction of macro quantities of iron (III) from 7.7 M hydrochloric acid solution. The analytical and instrumental parameters were optimised. The interference caused by some alloying elements is discussed. The bias of the analytical procedure and the accuracy of the proposed method were tested by means of "spiked" samples and standard reference materials of steels. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated for the investigated elements.

Key words: low-alloy steel, Se, Te, Pb, separation, ICP-AES

V prispevku je opisan postopek za simultano določevanje Te in Pb za koncentracijsko območje (5,0 - 100) $\mu g\ g^{-1}$ v malo legiranem jeklu z ICP-AES po predhodni ločitvi Fe in predkoncentriranju. Ločitev makrokoličin Fe(III) je potekala na osnovi ekstrakcije iz 7,7 M raztopine klorovodikove kisline. Izbrali smo optimalne analitske in operacijske razmere ter opisali interference elementov, ki so po ločitvi ostali v raztopini. Uspešnost ločitve in pravilnost metode smo ocenili z analizo internih dodatkov in certificiranih referenčnih materialov jekel. Za preiskovane elemente smo določili mejo detekcije (LOD) in mejo določevanja (LOQ).

Ključne besede: malo legirano jeklo, določitev Se,Te, Pb, ločitev, ICP-AES

1 INTRODUCTION

The quality of a steel can be influenced both positively and negatively by the presence of metallic or semi-metallic elements like antimony, arsenic, bismuth, selenium, tellurium, tin and lead. Trace levels of certain elements can accumulate in grain boundaries and weaken the microstructure. Traces of surface-active elements such as As, Sb, Se, Sn, Te and others can also affect both the hot- and cold-working properties of many steels and alloys deleteriously because of their tendency to accumulate in grain boundaries, thereby weakening the microstructure and influencing the magnetic properties of non-oriented steel sheets [1,2]. The catastrophic failure of critical components in high-stress, high-temperature, high-corrosion, or high-radiation applications can often be directly related to trace levels of certain impurities [3]. All these influences on the quality of steel are already detectable at very low concentrations (0.0002-0.02%).

The determination of trace levels of these elements is therefore very important and the development of a suitably sensitive method is necessary. Different techniques have been reported for determining trace amounts of selenium or tellurium, these include: neutron activation analysis (NAA), X-ray fluorescence spectrometry (XRF), spectrophotometry, voltametry [4], hydride-generation inductively-coupled-plasma atomic emission spectrometry (hydride-ICP-AES) [5], hydride-generation atomic absorption spectrometry (hydride-AAS) [6-9], and electro-thermal atomic absorption spectrometry (ET-AAS) [10-12]. Preconcentration methods have also been reported [13,14]. Selenium and tellurium can be separated simultaneously after reductive coprecipitation with palladium using ascorbic acid [4]. The determination of hydride-forming elements (As, Bi, Sn, Se, Te, Pb) in low-alloy steel was widely investigated, and HG AAS was suggested as a useful method [15-19]. Lead may be extracted into a methyl isobutyl ketone solution of tri-n-octylphosphine oxide (TOPO-MIBK) and the organic layer read out by flame atomic absorption [20,21]. High concentrations of iron can cause spectral interferences and increase the detection limit in the case of the ICP-AES technique [22]. The separation of iron [23] often has to be carried out in order to lower the detection limit.

In this paper a method for the extractive isolation of iron is proposed. Iron can be relatively easily extracted from 7,7 M hydrochloric acid solution prior to the determination of trace elements. Subsequent trace determinations are then free of interferences. The determination of Te and Pb that remained entirely in aqueous solution were free of interference and they were determined simultaneous using the ICP-AES method. Due to a lack of certified reference materials with such a low content of Te and Pb we also confirmed the accuracy by means of recovery.

2 EXPERIMENTAL

2.1 Apparatus

A Perkin Elmer, model OPTIMA 3100 RL, simultaneous inductively-coupled-plasma spectrometer was used. The emission intensity measurements were carried out in the conditions shown in **Table 1**. The calibration curve (0-10.0 µg mL^{-1}) for Se, Te and Pb was carried out with a multi-standard solution prepared from 1.0 mg mL^{-1} stock solutions of Se, Te and Pb in 2 % nitric acid solution.

Table 1: Operating parameters for the inductively-coupled-plasma spectrometer
Tabela 1: Operacijski pogoji delovanja atomskega emisijskega spektrometra z induktivno sklopljeno plazmo

SPECTROMETER	**PERKIN ELMER, simultaneous radial, model OPTIMA 3100 RL**
Frequency	40 MHz, free-running
Power output	1200 W
Output stability	< 0,1 %
ICP SOURCE	
Plasma torch	quartz / Al_2O_3 injector - 2 mm
Plasma argon flow	15 L min^{-1}
Auxiliary argon flow	0,5 L min^{-1}
Nebulizer argon flow	0,8 L min^{-1}
SAMPLE COMPARTMENT	
Spray chamber	Scott-type, Ryton
Nebulizer	Gem Type Cross-flow, pneumatic
Solution uptake rate	1 mL min^{-1}
Flush time	30 s
Signal integration time	10 s
Integration for determination	3

2.2 Reagents

The reagents were as follows: Pb standard solution (1.00mg L^{-1}), Se standard solution (1.00mg L^{-1}) and Te standard solution (1.00 mg L^{-1}): 100 mg of each metal was dissolved in HNO_3 (1+1), and diluted to 100 mL with water. A multi-standard solution of Pb, Se and Te was prepared from stock solutions before use. Distilled water was used for all the preparations of the standard and sample solutions. All the reagents used were of analytical grade. Nitric and hydrochloric acid were of p.a. quality (Merck). The di-isopropyl ether used for extraction was of p.a. quality (Carlo Erba).

2.3 Separation procedure

1, 3 or 5 g of Fe was carefully dissolved in 50 mL of hydrochloric acid (1+1) and oxidised with 5 mL of concentrated nitric acid. The multi-standard solutions of Se, Te and Pb (10.0 µg mL^{-1}) were "spiked" into solutions of iron. The spiked solutions were evaporated to the wet soils. 50 ml of 7.7 M hydrochloric acid was added to each spiked sample. When the soils were dissolved the solution was transferred to the separating funnel. The beaker was rinsed with 7.7 M hydrochloric acid and 35 mL of di-isopropyl ether was added. Solutions were shaken for 30 seconds. When aqueous and ether phases were separated the aqueous phase was transferred to another separating funnel. The extraction procedure was repeated three times for the 1 or 3g samples and four times for the 5g samples. The di iso-propyl ether phase with extracted iron was discarded and the water phase was transferred into a beaker. 1 mL of nitric acid was added and the solution was evaporated to less than 25 mL. The test solution was cooled and diluted to 25 mL in a volumetric flask.

The same procedure was used for the certified reference materials. The Si and C that remained in solution were filtered immediately after the dissolution of the chips.

2.4 Calibration

The calibration was carried out with a multi-standard solution in the range 0.5-10.0 µg mL^{-1} Se, Te and Pb. The blank values for the reagents were discarded and the concentration of the investigated elements that were determined in iron without the spike was negligible.

3 RESULT AND DISCUSSIONS

The interference effect of the Fe matrix on the simultaneous determination of Se, Te and Pb was substantially eliminated by the extraction of iron into the di iso-propyl ether. The efficiency of the extraction was >99 % for the 1 or 3 g samples, and in the case of the 5 g sample it was >95 %. Nitric acid was added at the stage of dissolving the sample and at the stage of evaporating the solution after extraction to minimise the Se losses. The spectral interferences caused by the alloying elements (Cr, Mo, Ni) that remained in solution after the extraction were checked up. The interferences free spectral lines for Se, Te and Pb determinations were chosen. The bias of the analytical procedure was investigated by means of a recovery study [24]. The different amounts of iron samples with spikes of different, but accurately known, amounts (C_{ref}) of investigated elements were analysed. The recovery ($R = C_{obs}/C_{ref}$) as a ratio of the observed concentration C_{obs} obtained by the application of an analytical procedure to a material containing analyte at a reference level C_{ref} and mean recovery ($\overline{\mathrm{Re}\ c}$) with standard deviation (s) was calculated (**Table 2**). The standard uncertainty was calculated as the standard deviation of the mean $u(\overline{\mathrm{Re}\ c}) = s/\sqrt{n}$. In a perfect separation R would be exactly unity. A significance test was used to determine whether the mean

Table 2: Bias estimations by means of recovery study
Tabela 2: Ocena odmika metode z uporabo izkoristka

Value	Element		
	Se	Te	Pb
$(\overline{\mathrm{Re}\;c})$ 1)[%]	74.3	93.9	98.0
s1)[%]	17.8	3.9	3.4
$u(\overline{\mathrm{Re}\;c})$	0.059	0.013	0.011
t	4.33	4.66	1.73

1) The mean $(\overline{\mathrm{Re}\;c})$ and sample standard deviation (s) are given as percentage recoveries.

Table 3: Accuracy assessment by means of certified reference materials
Tabela 3: Ocena pravilnosti z uporabo certificiranih referenčnih materialov

CRM	Se ($\mu g\ g^{-1}$)		Te ($\mu g\ g^{-1}$)		Pb ($\mu g\ g^{-1}$)	
	certified value	determined ± std.dev.	certified value	determined ± std.dev.	certified value	determined ± std.dev.
NBS 362	12[a]	9.6 ± 0.67	11[a]	8.7 ± 0.67	4.8	5.1 ± 0.61
NBS 363	1.6[a]	1.1 ± 0.25	9[a]	7.8 ± 0.35	19	17.8 ± 0.60
BS 2	n.d.[b]	< d.l.[c]	14	13.1 ± 0.34	20	19.1 ± 0.38

[a] value is not certified, but is given as approximate values for information
[b] not determined
[c] under detection limit

recovery was significantly different from unity. The test statistic t was calculated using equation 1.

$$t = \frac{\left|1-\overline{\mathrm{Re}\,c}\right|}{u(\overline{\mathrm{Re}\,c})} \tag{1}$$

This value was compared with the 2-tailed critical value t_{crit}, for n-1 degrees of freedom at 95 % confidence (where n is the number of results used to estimate $(\overline{\mathrm{Re}\;c})$. If t was greater than the critical value (t_{crit} = 2,26) then $(\overline{\mathrm{Re}\;c})$ is significantly different from 1. In this example a correction factor $1/(\overline{\mathrm{Re}\;c})$ should be used.

The accuracy of the method was also tested with some certified reference materials of steels (**Table 3**). The contents of Se, Te and Pb were sometimes only approximate. The limits of detection (LOD) for Te and Pb were 2 $\mu g\ g^{-1}$ and limits of quantification (LOQ) for Te and Pb were 4 $\mu g\ g^{-1}$.

4 CONCLUSIONS

Iron can be successfully removed by extraction into di iso-propyl ether. The interference that is caused by Cr that remains in solution after extraction can be overcome when the proper emission lines are chosen. The most sensitive spectral line for Se at 203,985 nm is free of interference. A strong interference is noticed for the Se determination at 203.990 nm, due to the presence of a small amount of Cr. The Cr spectral line at 238.574 nm interferes with the Te determination at 238.578 nm. Te is determined at 214.281 nm, and the spectral line at 220.353 nm is chosen for the Pb determination.

The results for the spiked samples are acceptable for the Pb determination, whereas the correction factor should be used for Te determination. Only a 74.3 % mean recovery is detected for the Se determination. The correction factor for the Se determination should not be applied, rather a wide investigation should be carried out.

Preliminary work showed that the method is not suitable for the Sn, Sb and As determinations because these elements form chloride compounds that are partly extractable into di-isopropyl ether.

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