

Določanje sledov kovin v jeklih in superzlitinah, po predhodni ločbi, s plamensko AAS

AAS Determination of Trace Metals in Steels and Superalloys with Preliminary Separation

T. Lavrič*, A. Osojnik*, Z. Kristan*

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Delo opisuje primerjalno študijo ločbe ionsko asociiranih kompleksov Ag, Bi, Cd, Pb, Se, Sn, Te in Zn s trioktilfosfinskim (TOPO) in trioktilaminom (TOA) v metilzobutylketonu (MIBK). Raziskujemo možnost uporabe obeh skupinskih ločb naštetih kovin za določanje nečistoč v jeklih in superzlitinah na osnovi niklja, s končnim določanjem s plamensko AAS. Separiranje in določanje preverjamo s certificiranimi referenčnimi materiali. Zbrani so tudi podatki analize sledov za nikljeve zlitine iz proizvodnje in podatki o občutljivosti, točnosti, ponovljivosti določanja ter o praktični meji zaznavnosti za vsak element.

UVOD

Sledovi Ag, Bi, Cd, Pb, Se, Sn, Te in Zn ter še nekaterih elementov vplivajo kvarno na mehanske, fizikalne in tehnološke lastnosti litega železa, nekaterih vrst jekla, predvsem pa so škodljivi v superzlitinah, ki se uporabljajo pri visokih temperaturah. Nezaželjene in škodljive so že primesi reda velikosti nekaj ppm ($=\mu\text{g g}^{-1}$) in manj. Pravilna ocena takih količin zahteva precizne metode določanja, ki so vezane izključno na instrumentalno tehniko. Vendar so redke in zelo drage tiste tehnike, ki imajo, brez predkoncentriranja, zadostno občutljivost za direktno analizo sledov kovin in da so, istočasno brez predhodne ločbe sledov od matrice, proste motenj glavnih komponent. Plamenska AAS, neplamenska AAS in ICP-AES zahtevajo ločbo ter skoncentriranje ppm količin kovin od osnove z namenom, da se odstranijo motnje ali/in zaradi izboljšave parametrov določanja. Primerne tehnike so ekstrakcija, hidridna tehnika, soobarjanje, redukcija do elementarnega stanja. Na izbiro ločbe vplivajo fizikalne in kemične lastnosti določenega elementa in matrice, kar vpliva tudi na to, ali je ločba lahko eno-ali večelementna.

Namen predstavljene študije je bil zbrati podatke o možnosti skupinske ločbe in skoncentriranja ppm količin jodidov Ag, Bi, Cd, Pb, Se, Sn, Te in Zn iz večje zatehte jekla oziroma superzlitine na nikljevi osnovi v 5, 10 ali 20 ml organske faze TOPO-MIBK ali TOA-MIBK. Kontrola ločbe je potekala z analizo organskih ekstraktov s pla-

The present work describes a comparison study of the separation of Ag, Bi, Cd, Pb, Se, Sn, Te and Zn, as iodide complexes ion-associated with trioctylphosphine-oxid (TOPO) and with trioctylamine (TOA), into methylisobutylketon (MIBK).

The efficiency of both multielement separations, followed by flame AAS determination, was investigated to determine the traces of analytes in different grade of steels and superalloys. Standard reference materials were used to test separation and determination. The sensitivity, accuracy and repeatability data, and also the practical limit of detection for each element are gathered and assessed.

INTRODUCTION

Mechanical, physical and technological properties of various types of cast iron, some low alloy steels, and especially superalloys for high temperature application strongly depended on trace metal contents such as Ag, Bi, Cd, Pb, Se, Sn, Te, Zn, and others. Because of their harmful effect already at the ppm ($=\mu\text{g g}^{-1}$) level and lower a great attention has been paid to the knowledge of ppm concentrations of trace elements. All that requires reliable, correct methods of determination, that are exclusively connected with instrumental techniques. Except a few and expensive techniques have satisfactory sensitivity for direct determination of trace metals without preconcentration and that they are at the same time free of interferences of the matrix without separation. The conventional flame AAS, flameless AAS, ICP-AES demand the separation and preconcentration of ppm amounts of metals from the matrix in order to avoid interferences or/and to improve parameters of determination. The convenient separation methods are solvent extraction, hydride generation, coprecipitation, reduction to elemental state. The possibility of application of these separation methods depends on physical and chemical properties of the determined trace and of the matrix, what influences also to one-or multielement separation.

The aim of the present study was to gather analytical data obtained by the use of preconcentration solvent extraction technique of iodides of Ag, Bi, Cd, Pb, Se, Sn, Te, and Zn from large weight from various kinds of steels and superalloys on nickel base by the use of 5, 10, 20 ml TOPO-MIBK and TOA-MIBK organic phase, followed by

* SŽ — Metalurški inštitut

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mensko AAS. Uvedli smo TOPO-MIBK ločbo po Burkeju^{1,2}, ki jo uporablja avtor za določanje Bi, Pb, Sb in Sn v aluminiju, železu in nikljevih zlitinah. Janoušek³ in Staats⁴ uporabljata podobno ločbo za določanje mikroelementov v jeklih. Janoušek določa le Bi, Pb, Sb in Sn v nelegiranem jeklu, medtem ko je Staats prilagodil ločbo določanju Cu, Zn, Mo, Ag, Sn, Sb, Pb in Bi za nelegirana in malolegirana jekla. Ločba TOA-MIBK je manj v rabi na področju analize jekla^{5,6}, bolj za posamezne elemente sledove v bakru, svincu in selenu^{7,8,9}. Dodatno smo izvedli primerjalno študijo določanja Te z redukcijo do elementarnega Te. Opisane so separacijske metode in predstavljeni rezultati za certificirane referenčne materiale (CRM) ter nekaj nikljevih zlitin iz proizvodnje. V možnih primerih smo izvedli za CRM primerjavo z dosegljivimi podatki drugih avtorjev.

EKSPERIMENTALNI DEL

Aparatura

Meritve smo izvajali z AA spektrometrom Perkin Elmer model 2380, ki je bil opremljen z zunanjo izvorom za brezelektrodne žarnice. Za določanje Bi, Se, Sn in Te smo uporabljali kot primarni izvor svetlobe brezelektrodne žarnice, za določanje Ag, Cd, Pb in Zn pa votle katode. Signale smo beležili na printerju Perkin Elmer PRS-10. Za vsak element smo optimirali lego gorilca in parametre plamena na maksimalno absorbanco z razprševanjem standarda v ustreznem ekstraktu. Za vse elemente smo uporabljali plamen zrak-acetilen in »impact bead«, le za Sn plamen didušikov oksid-acetilen in »vetnico«. Čas integracije je bil vedno 1 sec pri hitrosti razprševanja organske faze ~ 5 ml min⁻¹. Meritve smo izvajali za vsak element na njegovi najbolj občutljivi-resonančni liniji. Meritve smo izvajali za vse elemente izključno samo v linearnem območju, kjer je zadoščalo umerjanje z enim standardom, čeprav je instrument sposoben sprejeti tri standarde za umerjanje in korekturo krivulje.

Reagenti in materiali

Vse kemikalije so bile nabavljene pri fa. Fluka. MIBK in kisline so bile p.a., TOA purum kvalitete. Uporabljali smo 5 % raztopino TOPO v MIBK in enako 5 % TOA v MIBK. Za pripravo vzorcev smo uporabljali sigradur čaše. Uporabljali smo CRM naslednjih dobaviteljev: BAS, NBS in MBH. Večina jih je bila kupljena v obliki finih ostružkov, nekateri v obliki diskov (MBH), iz katerih smo pripravili ostružke z ene strani diska. Kemična sestava uporabljenih CRM je razvidna iz **tabele 1**.

Postopki za jekla in nikljeve zlitine

Opisana sta dva postopka ekstrakcije Ag, Bi, Cd, Pb, Se, Sn, Te in Zn ter en postopek redukcije Te. Vsem trem so skupne tri faze: raztapljanje s pripravo vzorca, ločba in zadovoljivo določanje. Vsaj en slepi vzorec pridružimo vsakemu postopku.

— **TOPO-MIBK ekstrakcija:** Osnova postopka je ekstrakcija jodidov enega ali več elementov, kot jo navaja Burke¹, z umerjanjem z raztopinami, ki jih vodimo skozi celoten postopek². Vzorec jekla ali nikljeve zlitine (1–5 g, odvisno od vsebnosti sledov) počasi in previdno raztopimo v 3 + 1 mešanici HCl + HNO₃. Raztopino izparimo na ~ 5 ml, dodamo 10 ml HCl, razkrojimo HNO₃ z mravljično kislino. Raztopino izparimo do goste sirupaste konsistence, da izženemo vse dušikove okside in da se razkroji mravljična kislina. Dodamo HCl, askorbinsko

flame AAS. We followed the TOPO-MIBK separation of Burke^{1,2}, applied by author for Bi, Pb, Sb, and Sn determination in aluminium, iron and nickel base alloys. Janoušek³ and Staats⁴ performed similar separation for determination of trace elements in steels. Janoušek³ determined Bi, Pb, Sb, and Sn in unalloyed steel but Staats⁴ adapted separation for the determination of Cu, Zn, Mo, Ag, Sn, Sb, Pb, and Bi for unalloyed and low alloyed steels. The TOA-MIBK extraction is a little applied separation for steels^{5,6} but more for the determination of single elements in copper, lead, and selenium^{7,8,9}. For Te also a comparison with reduction to elemental Te was made. Methods of separation are shortly described and the results presented for the analytes of certified reference materials (CRMs) and elected nickel base alloys from production. Some results for CRMs are compared with available literature data.

EXPERIMENTAL

Instrumentation

Perkin Elmer atomic absorption spectrometer Model 2380, equipped with an external electrodeless discharge power supply was used. As primary light source electrodeless discharge lamps were employed for the determination of Bi, Se, Sn, Te, and for the determination of Ag, Cd, Pb, and Zn hollow cathode lamps were used. The signals were printed on a Perkin Elmer PRS-10 printer. Other conditions were as follows: the burner position and flame parameters for each element were optimized for maximum absorbance by aspirating standard organic solution. The impact bead and air-acetylene flame were used for all test analytes, except for Sn nitrous oxide-acetylene and spoiler were used. Integration times of 1 sec were used in all cases in conjunction with an aspiration time ~ 5 ml min⁻¹ of organic solution. The most sensitive-resonance line was chosen for each element. The measurements were made for all analytes exclusively in the linear concentration range where the calibration with one standard was sufficient, otherwise the instrument is capable of accepting up to three standards for calibration and curve correction.

Reagents and materials

All analytical work reagents were supplied from Fluka, MIBK and acids p.a. grade, TOPO puriss, and TOA purum grade. TOPO-5 % solution in MIBK, TOA-5 % solution in MIBK was applied. Sigradur vessels were used for sample preparation. Certified Reference Materials (CRMs) supplied by the BAS, NBS and MBH were used. The most of them were supplied in finely divided form, but some of them were in disc form (MBH). From discs fine drillings were cut on one side **Table 1**.

Procedures for steels and nickel base alloys

Two solvent extraction methods for determination of Ag, Bi, Cd, Pb, Se, Sn, Te, and Zn are described, and one procedure for reduction of Te.

All three further described procedures have three steps in common: dissolution with pretreatment of the sample, separation, and satisfactory determination. A blank was included in each of the following digestion procedures:

— **TOPO-MIBK extraction:** Procedure based on the extraction of iodides of one or more elements re-

Tabela 1: Opis uporabljenih standardnih referenčnih materialov in podatki za Ag, Bi, Cd, Pb, Se, Sn, Te ter Zn
Table 1: Description of standard reference materials used, and data for Ag, Bi, Cd, Pb, Se, Sn, Te and Zn

Oznaka vzorca Sample identification	Vrednosti v certifikatih ($\mu\text{g g}^{-1} = \text{ppm}$) / Values of certificates ($\mu\text{g g}^{-1} = \text{ppm}$)						
	Ag	Bi	Cd	Pb	Se	Sn	Te
EURO 085-1							
NBS 365	(-20 ppb)	(<0.1)	ND	0.19	(<0.1)	(0.2)	(<0.1)
NBS 361	4	(4)	ND	0.25	(40)	100	(6)
NBS 362	11	(20)	ND	4.8	(12)	160	(11)
NBS 363	37	(8)	ND	18.6	(1.6)	1040	(9)
BCS 345	<0.2 [$<0.5 - 0.2$] ₁₁	<0.2 [$<0.05 - <0.2$] ₁₀	<0.1 [$<0.05 - <0.1$] ₈	0.2 $\pm$ 0.05 [$0.12 - 0.30$] ₈	<0.5 [$<0.2 - <0.5$] ₇	6 $\pm$ 1.6 [$3.8 - 8.0$] ₈	<0.2 [$<0.05 - <0.2$] ₉
BCS 346	35 $\pm$ 2 [$32.2 - 38.1$] ₁₃	10 $\pm$ 1 [$9.4 - 11.6$] ₁₃	0.4 $\pm$ 0.05 [$0.34 - 0.48$] ₅	21 $\pm$ 2 [$18 - 23.2$] ₁₄	9 $\pm$ 1 [$7.5 - 10.2$] ₇	91 $\pm$ 7 [$78 - 100$] ₇	12 $\pm$ 1 [$9.5 - 14.5$] ₁₀
MBH 11980D	<2	<0.1	<0.1	<2	<5	<10	<2
MBH 11980F	0.2	<1.5	0.1	3	<1	18	<0.2
MBH 11980A	20	2	0.2	10	15	40	12
							25 $\pm$ 6 [$18 - 42$] ₁₅
							<0.1
							(1)
							(5)
							(4)
							<0.5 [$0.3 - <0.5$] ₇
							29 $\pm$ 2 [$25.7 - 31.5$] ₈
							<2
							6
							15

Euro: 085-1, nelegirano jeklo/unalloyed steel

NBS: 361, 363 malo legirano jeklo/low alloy steels

NBS: 365 elektrolitsko železo/electrolytic iron

BCS: 345, 346 -IN 100 zlitine/IN 100 alloys

MBH: 11980D, 11980F, 11982A-IN 100 zlitine/IN 100 alloys

(): Vrednosti niso certificirane/Values are not certified

[]: Določitve v certifikatu v mejah/ Determination in certificat within the limit, x število določitev/number of determinations.

N.D.: ni določeno/not determined.

kislino in jodidni reagent ter ekstrahiramo v 5, 10, 20 ali 30 ml 5 % TOPO v MIBK. Čas ekstrakcije je 30 sek. Organsko fazo razpršimo v plamen. Za določitev enega samega elementa zadostuje 5 ml ekstrakta. Izkušen analitik lahko določi vseh osem elementov iz 30 ml ekstrakta.

Podrobni eksperimentalni podatki kot tudi diskusija k TOPO-MIBK ekstrakciji so na voljo v literaturi^{1,2}. Pri naših poskusih smo povečali količino zmesne kisline za raztapljanje 5 g vzorca iz 60 na 100 ml.

2— TOA-MIBK ekstrakcija: Priprava vzorca in ločba sta povsem enaki kot za TOPO-MIBK ekstrakcijo, le da smo uporabljali kot ekstraktant 5 % TOA v MIBK, čas ekstrakcije je daljši 5 min.

— Redukcija Te do elementarnega stanja s hidrazinhidrokloridom: Priprava vzorca je enaka kot opisujemo spredaj do vključno z dodatkom mravljinčne kisline. Nato dodamo ~ 25 ml HCl ter razredčimo na ~ 200 ml. Kislost raztopine naj bo 2—3 M. Dodamo dvojno količino hidrazinhidroklorida, glede na zatehto vzorca. Postavimo na vodno kopel pri 100 °C za 30 min, da se pojavi črna oborina izpadlega Te, nato pustimo čašo z oborino nadaljnjih 30 min poleg vroče plošče. Koagulirano oborino zberemo na milipor filtru 0.2 µm, speremo z vodo in raztopimo v čimmanj hladne HNO₃, ohladimo, dodamo 5 ml HCl, razredčimo na 25 ml, razpršimo v plamen.

REZULTATI IN DISKUSIJA

Umerjanje in meritve

Za umerjanje aparature smo sprva v glavnem uporabljali CRM, ki smo jih pripravljali na enak način kot vzorce. Zaradi pomanjkanja CRM s ppm vsebnostjo iskanih elementov smo včasih naredili referenčne vzorce, že pred raztapljanjem, z združevanjem elektrolitskega železa (NBS 365) ali zelo čiste nikljeve zlitine (BCS 354) z različnimi CRM v različnih utežnih razmerjih.

Nadalje smo pripravljali raztopine za umerjanje iz standardnih raztopin, ki smo jih dodajali elektrolitskemu železu (NBS 365) ali superzlitini (BCS 345). Standardne raztopine smo vedno dodali šele po raztopitvi matrice. Tako pripravljene sintetske vzorce smo vodili skozi celoten postopek. Vse standardne raztopine smo pripravili iz čistih kovin ali p.a. soli (Ag). Z obema načinoma umerjanja dobimo skoraj identične rezultate za vse elemente, razen za Bi, kjer smo ugotovili, da dobimo pravilne rezultate le z umerjanjem s CRM; z umerjanjem s sintetskimi vzorci dobimo pre nizke rezultate.

Pravilno umerjanje je zelo važen dejavnik celotnega postopka. Kritična točka je v pravilni izbiri ničle instrumenta. Kot ničlo instrumenta vstavimo vedno elektrolitsko železo (NBS 365) ali nikljevo zlitino (BCS 345), ki jo v nadaljnjem imenujemo delovna slepa raztopina in jo pripravimo enako kot vzorce. Dobljeni rezultati so namreč pokazali, da dobimo napačne rezultate, če vstavimo kot ničlo čisti MIBK, izmerimo koncentracijo delovne slepe raztopine in to vrednost naknadno odštevamo od celotne vrednosti za umerjalni standard ali preiskovani vzorec. Delovno slepo raztopino pripravimo za vsako skupino vzorcev in jo obvezno uporabljamo za izpiranje med posameznimi vzorci, posebno kadar merimo v bližini praktične meje zaznavnosti in pri ogrevanju gorilca.

Uporabnost obeh ekstrakcijskih sistemov

Meritve Ag, Bi, Cd, Pb, Se, Sn, in Te v TOPO-MIBK in TOA-MIBK ekstraktih so pokazale podobno učinkovitost ločbe v obeh sistemih, medtem ko se Zn ekstrahira dobro le v TOPO-MIBK, v TOA-MIBK največ 50 %, pri izbranih delovnih pogojih. Izkoristki ločb so za vse ostale ele-

ported by Burke¹, with calibration solutions that have been taken through extraction procedure², was applied. The sample of steel or nickel base alloy (1—5 g depending on amount of traces) slowly and carefully was dissolved to avoid losses by sputtering in 3+1 mixture of HCl+HNO₃. The resulting solution was then evaporated to ~ 5 ml, then 10 ml HCl was added, and nitric acid decomposed by formic acid. The solution was then evaporated nearly to dryness to sthick consistence drive off to all nitrogen oxide fumes and finally destroying of formic acid. After the addition of HCl, ascorbic acid, and iodide reagent, the extraction into 5, 10, 20 or 30 ml of 5 % TOPO-MIBK followed, extraction time 30 sec. The organic extract was aspirated into flame. For determination of one element only 5 ml of extract satisfy. An experienced analyst is able to determine all eight analytes from 30 ml of extract. Data for experimental conditions as well as discussion on the TOPO-MIBK separation may be found in the literature^{1,2}. In our research acid mixture was increased for 5 g sample from 60 to 100 ml.

— TOA-MIBK extraction: The preparation of the sample and separation procedure are the same as under TOPO-MIBK extraction, except we added 5 % TOA in MIBK instead of TOPO the extraction time was 5 min.

— Reduction of Te to elemental state by hydrazine hydrochloride: The dissolution procedure as described above, inclusive of formic acid addition. After that hydrochloric acid was added to adjust the acidity to 2—3 M and the volume to ~ 200 ml (~ 25 ml concentrated hydrochloric acid/200 ml). Double amounts of hydrazine hydrochloride was added with regard to the sample weight. The mixture was incubated in a water bath at 100 °C for 30 min till black precipitate of Te appeared. The mixture was allowed to stand near the hot plate further 30 min. Coagulated precipitate was collected on a millipor filter 0.2 µm, washed with water and dissolved in a few ml of cold concentrated nitric acid, cooled, 5 ml of hydrochloric acid was added, diluted to 25 ml and applied to AAS.

RESULTS AND DISCUSSION

Calibration and measurements

In the first stage calibration solutions from CRMs were used for calibration of the instrument, which were prepared on the same way as the samples. To overcome the lack of standards with ppm amounts of analytes, reference materials were sometimes prepared with known amounts of traces by spiking electrolytic iron (NBS 365) or very clean nickel base alloy (BCS 345) with different CRMs in different proportions before the dissolution step.

Later also calibration solutions from varying amounts of a stock solution of respective element and electrolytic iron (NBS 365) or superalloy (BCS 345) were prepared. The stock solutions were added always after dissolution of the matrix. All standard solutions were prepared from clean metals or p.a. salts (Ag).

With both calibration made we achieved nearly identical results for all elements. Except for Bi we stated, that correct results were obtained with calibration with CRMs. Calibration with synthetic standards yields to low results.

The calibration is an important factor in all procedures. A critical point in both liquid-extraction procedures was imposed by correct choice of the zero of the instrument. The working blanc, electrolytic iron or very clean nickel base alloy taken through all procedure,

mente v obeh sistemih med 85—110 %. Če upoštevamo nizke koncentracije, lahko ugotovimo, da so izkoristki dobri.

Oba ekstrakcijska sistema sta uporabna za analizo sledov v jeklih in nikljevih zlitinah.

Prednost ločbe s TOPO-MIBK so: je izrazita večelementna ločba sledov, ki omogoča tudi določanje Zn po opisanem postopku. Odlikuje jo kratek čas ekstrakcije (30 sek) v primerjavi s 5 min ekstrakcije s TOA-MIBK.

Prednost ločbe s TOA-MIBK so: je tudi večelementna ločba, ki bi bila morda ob drugačnih pogojih preiskovane raztopine uspešna tudi za Zn. Nihanje ozadja je manj izrazito kot pri TOPO-MIBK, kar pride posebno do izraza pri Se, ki je težko določljiv s plamensko AAS, za katerega dobimo s TOA-MIBK stabilnejše odčitke za slepi vzorec in vzorec, s tem v zvezi boljši standardni odmik, kar je posebno važno, ko določamo koncentracije v bližini praktične meje zaznavnosti. Standardni odmik desetih meritev istega vzorca za $0,2 \mu\text{g ml}^{-1}$ Se je bil v TOPO-MIBK 15—25 %, v TOA-MIBK 10—20 %.

Meritve občutljivosti za TOPO-MIBK in TOA-MIBK ekstrakte dajejo približno enake vrednosti za vse elemente, z izjemo Sn, kjer je razlika med obema sistemoma občutnejša, **tabela 2**. Na splošno je občutljivost do-

ločanja dobra, najslabša je za Sn. V primerjavi s klorovo *must be set as zero of the instrument used in this study. The results obtained confirmed, that it is wrong to measure the concentration of the working blank against clean MIBK separately, and subsequent its subtraction from the total signal for calibration sample and tested sample.*

A working blank should be prepared with each set of samples, and may be used obligatory for washing out between each sample, particularly by measuring near the practical limit of detection, and for burner warm up.

Application of extraction systems

Measurements of Ag, Bi, Cd, Pb, Se, Sn, and Te in TOPO-MIBK and TOA-MIBK extracts yield approximately the same degree of separation; for Zn only the extraction into TOPO-MIBK is convenient, the extraction in TOA-MIBK is less than 50 %, under chosen working conditions. 85—110 % recoveries for all analytes were afforded. Considering the low concentrations the recoveries can be regarded as acceptable. The both extraction systems are available for the analysis of trace elements, mentioned above, in steels and nickel base alloys. Advantages of TOPO-MIBK separation are: it is an expensive multielement separation technic, that hat is unable to separate and preconcentrate also Zn, under described procedure. The separation is distinguished by less time consuming for shaking, 30 sec against 5 min for TOA-MIBK. Advantages of TOA-MIBK separation are: is also a multielement separation technic, which could be useful also for Zn in other conditions of the working solution. The fluctuation of the signals of the background is smaller than of TOPO-MIBK solutions which contributes to slightly more stable signals. This is especially evident for Se, which is difficult to determine in TOPO-MIBK. This contributes to stable signals for working blank and sample solution and lower relative standard deviation, which is especially noticeable when concentrations are near the practical detection limit. Relative standard deviation for ten measurements of one sample on $0,2 \mu\text{g ml}^{-1}$ level of Se was approximately 15—25 % in the TOPO-MIBK, and 10—20 % in the TOA-MIBK solution.

Measurements of sensitivity of determination for all analytes in both solvent extraction procedures were nearly the same, with exception for Sn, where the difference is grater. Generally the sensitivity of determination is good except for Sn. The effects of enhanced sensitivity of the analytes in organic phases compared with $\text{H}_2\text{O} + \text{HCl}$ solutions are shown in **Table 2**. Proportional improvements in sensitivity realise better practical detection limits. Practical detection limits, the lowest concentration which can be determined under routine conditions, based on 5 g sample and 5 ml organic extract are shown in Table 3.

All measurments were made for all analytes exclusively in linear concentration range shown in **Table 3**.

Repeatability test chiefly indicated a relative standard deviation of 2 % at about $100 \mu\text{g g}^{-1}$ level, 10 % at about $6 \mu\text{g g}^{-1}$ level and 20—30 % at about $2 \mu\text{g g}^{-1}$ level within different batches on different days. Recommended procedures gave good reproducibility for the same organic extract from day to day for all analytes.

Application of reduction procedure for tellurium

As can be seen from **Table 4**, the Te is determined enough precisely by the reduction method to elemental

Tabela 2: Vpliv TOPO- in TOA-MIBK ter $\text{H}_2\text{O} + \text{HCL}$ sistemov na občutljivost določanja.

Table 2: Effect of TOPO- or TOA-MIBK, and $\text{H}_2\text{O} + \text{HCL}$ systems on the sensitivity of determination

Element	$\mu\text{g ml}^{-1}$	Absorbanca/ Absorbance		
		TOPO-MIBK	TOA-MIBK	$\text{H}_2\text{O} + \text{HCL}$
Ag	0.5	0.166	0.178	0.062
Bi	3.0	0.178	0.168	0.058
Cd	0.5	0.238	0.238	0.120
Pb	3.0	0.202	0.204	0.094
Se	3.0	0.044	0.036	0.014
Sn	10.0	0.040	0.027	0.012
Te	3.0	0.126	0.114	0.046
Zn	0.2	0.258	/	0.072

Tabela 3: Praktične meje zaznavnosti in ugotovljena linearna območja umerjanja v organskem sistemu.

Table 3: Practical limits of detection and linear ranges of calibration in organic system.

Element	Praktična meja zaznavnosti Practical detection limit		Območje linearnosti Range of linear response ($\mu\text{g ml}^{-1}$) ^b
	($\mu\text{g g}^{-1}$) ^{a,b}	(%)	
Ag	0.2	2×10^{-5}	0.05—3.0
Bi	0.4	4×10^{-5}	0.2—6.0
Cd	0.1	1×10^{-5}	0.1—0.5
Pb	0.4	4×10^{-5}	0.2—4.5
Se	1.0	1×10^{-4}	0.5—3.0
Sn	1.0	1×10^{-4}	1 —50
Te	0.4	4×10^{-5}	0.2—6.0
Zn	0.05	5×10^{-6}	0.2—0.6

^a — Pri teži vzorca 5g, ekstrakt 5 ml
Using 5g sample, extract 5 ml

^b — Vse vrednosti so približno enake za TOPO- in TOA-MIBK, z izjemo za Zn
All values are approximately equal for TOPO- and TOA-MIBK, exceptly for Zn

Tabela 4: Rezultati določanja Ag, Bi, Cd, Pb, Se, Sn, Te in Zn v CRM ($\mu\text{g g}^{-1}$)
Tabelle 4: Results of Ag, Bi, Cd, Pb, Se, Sn, Te and Zn determination on CRM_s

Element	EURO 851-1		NBS 361		NBS 362		NBS 363		BCS 345		BCS 346		MBH 11980D		MBH 11980F		MBH 11982A	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Ag	a	(4)	4.2±0.41	(11)	12.8				<0.2	0.13±0.06	35	34.2±1.7	<2	0.5±0.3	0.2	0.2	20.6±1.0	
	b		4.1±0.36						0.16±0.04			33.7±2.4		<0.2		0.2	20.5±1.0	
	d		4.0 ^e		10.6 ^e													
Bi	a	(4)	4.4±0.6	(20)	19.8±2	8	5.4±0.7		<0.2	<0.2	10	9.9±0.9	<0.1	<0.4		2	1.8	
	b		4.2±0.4		19.1		7.1±0.6		<0.2			9.7±1.2		<0.3			1.9	
	d		5.3 ^e , 5'		26 ^e , 30'		6.4 ^e , 8'											
Cd	a	N.D.	<0.1	N.D.	<0.1	N.D.	<0.1	<0.1	<0.1	<0.1	0.4	0.38±0.05	N.D.	0.1	0.08			
	b		<0.1		<0.1		<0.1		<0.1			0.37±0.05		0.09				
	d		<0.1 ^e		<0.1 ^e		<0.1 ^e											
Pb	a	0.25	<0.3	4.8	5.1±0.8	18.6	18.2		<0.6	<0.6	21	20.7±1.5	<2	<2		10	11.3±1.5	
	b		<0.4		4.6		18.5		<0.6			20.6±0.8		<2			11.2±1.5	
	d		<0.2 ^e		4.4 ^e		18.7 ^e											
Se	a	(40)	39.9±1.8	(12)	10±0.8	(1.6)	2.2±0.4		9			9.6±1.3	<1	0.97±0.2	15	14.7±1.7		
	b		40.6±1.7		10.1±0.7		3.1±0.8											
	d		34'		13'		1'											
Sn	a	100	103±16.5				6		5.3±0.8	91	89.2±4.1				40	41.3±3.0		
	b		99.9±3						6.1±0.5		94.0±2.5					40.2±2.0		
	d		93.9 ^e , 90'															
Te	a	(6)	5.9±0.2	(11)	10.2±0.7	(9)	9.6±1.0		<0.2	<0.5	12	12±1.6	<2	<1	12	13.6±0.7		
	b		5.5±0.2		10.7		9.2		<0.5					<1		13.7±1.2		
	c		6.3±1.5		9.5±0.5		10.7±1.3					13±1.2				14.0		
	d		4'		8'		7'											
Zn	a	25	21.8±3.5	(1)	N.D.	(5)	4.9±1.6	(4)	<0.5	<0.7	29	29.5±4.5	<1	40	6	7.0±1.6	N.D.	
	d		24.3 ^e		1.6 ^e		5.3 ^e						(?)					

A — Vrednosti v certifikatih/Values of certificates

B — Naši rezultati/Our results

a — TOPO-MIBK; b — TOA-MIBK; c — redukcija Te/Values not certified

() — Vrednosti niso certificirane/Values not certified

± ... Standardni odklik $n \geq 8$ /Standard deviation $n \geq 8$

d — Literaturni podatki/Literature data: e — TOPO-MIBK (Lit. 4); f — hidrid/hydrid-AAS (Lit. 10)

Tabela 5: Rezultati analize elementov-sledov v raznih vzorcih iz proizvodnje.
Table 5: Analytical results of trace elements for various samples from production.

Vzorec Sample	Vsebnost/ Content ($\mu\text{g g}^{-1}$ = ppm)							
	Ag	Bi	Cd	Pb	Se	Sn	Te	Zn
Aluminij Aluminium	<3	<1	0.24	160	1.2	17.4	0.6	39
Nikelj Nickel	0.8	<1	0.05	12.4	2.7	15.6	0.8	5
Kobalt Cobalt	1.5	<1	11.1	5.9	2.9	4.3	0.7	12
Krom Chromium	1.7	<1	0.04	20.5	2.1	2.0	0.9	2.4
Titan Titanium	6.9	<1	0.15	<1	18.7	220	5.6	3
Molibden Molybdenum	1.9	<1	0.13	5.1	4.5	20.0	2.4	0.08
NIMONIC 263/1 ^a	0.24	0.2	0.12	2.9	2.3	14.0	1.3	2.4
NIMONIC 263/2 ^a	0.20	<1	0.10	5.5	2.0	11.4	0.46	15.5
NIMONIC 263/3 ^a	0.28	<1	0.10	7.2	1.8	11.2	0.70	32
INCONEL ^b	0.89	5.5 $\pm$ 0.5 ^c (7)	0.16	33.7 $\pm$ 3.5(7)	3.9	96.8	2.1	13.6

^a— Ni-zlitina: 50%Ni, 20%Co, 20%Cr, 5.9%Mo, 2.5%Ti, 0.36%Al, 0.65%Fe
Ni-alloy

^b— Ni-Fe zlitina: 55%Ni, 18%Cr, 0.3%Co, 16.6%Fe, 2.8%Mo, 5%Nb, 0.6%Al, 1.0%Ti
Ni-Fe alloy

^c— Srednja vrednost $\pm$ standardni odklik od sr. vr. (n=7)
Mean $\pm$ standard deviation of the mean (n=7)

dikovo kislimi raztopinami se v organskih sistemih poveča občutljivost od 2.5 do 3-krat.

Praktične meje zaznavnosti, t.j. najnižja koncentracija, ki smo jo še lahko določili z rutinskim delom, pri uporabi 5 g zatehte vzorca in 10 ml organskega ekstrakta, so razvidne iz **tabele 3**.

Vse meritve smo izvajali za vse elemente samo v linearnih območjih, ki jih navajamo v **tabeli 3**.

Test ponovljivosti daje relativni standardni odklik 2 % na nivoju 100 $\mu\text{g g}^{-1}$, 10 % na nivoju 6 $\mu\text{g g}^{-1}$ in 20–30 % na nivoju 2 $\mu\text{g g}^{-1}$, in to glede na vzorce, ki so bili pripravljene ob različnih dnevih. Postopka, ki ju priporočamo, dajeta za vse elemente dobro ponovljivost istega organskega ekstrakta v več zaporednih dnevih.

Uporabnost postopka redukcije telurja

Kot je razvidno iz **tabele 4**, se da Te določati dovolj točno z metodo redukcije do elementarnega stanja, ki ji sledi določanje z AAS iz $\text{H}_2\text{O} + \text{HCl}$ raztopin.

Na splošno dosegamo dobra ujemanja s CRM v širokem koncentracijskem območju. Občutljivost in praktična meja zaznavnosti sta slabši v primerjavi z organskimi raztopinami. Meja zaznavnosti je 6 $\mu\text{g g}^{-1}$. Postopek je uporaben tako za analizo jekla kot zlitine na osnovi niklja.

Analiza certificiranih referenčnih materialov

Z namenom, da bi preverili pravilnost ločbe in skoncentriranja, smo analizirali večje število CRM. Vrednosti, dobljene za vrsto standardov jekel in nikljevih zlitin, se zadovoljivo ujemajo s certificiranimi vrednostmi, kar potrjuje, da se da doseči z opisanima postopkoma ločbe

state, followed by AAS determination of $\text{H}_2\text{O} + \text{HCl}$ solutions. In general, there is a good agreement with CRMs over a wide concentration range, but the sensitivity and the practical detection limit are poorer, than for the organic solutions. The limit is 6 $\mu\text{g g}^{-1}$. The procedure is available for the analysis of steels and nickel base alloys.

Analysis of certified reference materials

To assess the accuracy of the separation and preconcentration methods many CRMs were applied. The values obtained for a range of standard steels and nickel base alloys show close agreement with certified values for applied procedures, confirm a good enrichment factor and also prove that accurate results can be obtained at ppm level. The results are given in Table 4 together with those obtained by other investigators from literature. Recoveries are usually higher than 85 %. The determined values are for some CRMs higher and for some lower when compared with the certificate. It is interesting to note that also the data in certificates are in a spread, and that some values are not certified but only given for information.

Analysis of samples from production

The established methods are applied on the sample from production, see Table 5.

There was problem with dissolution of nickel base alloy with 5 % Nb. In this case the addition of H_2SO_4 was not sufficient, but the addition of 1 ml HF prior or after the dissolution of the sample was successful.

dobro skoncentriranje sledov in pravilne rezultate na ppm nivoju. Rezultate navajamo v tabeli 4, skupaj s podatki drugih avtorjev, ki smo jih zasledili v literaturi. Izkoristki so običajno večji od 85 %. Nekatere naše vrednosti so včasih višje, drugič nižje v primerjavi s certifikati. Opozoriti je treba, da se tudi v certifikatih gibljejo analizne vrednosti v določenih razponih, nekatere vrednosti celo niso certificirane, ampak dane le v vednost.

Analiza vzorcev iz proizvodnje

Vpeljane metode uporabljamo za analizo vzorcev iz proizvodnje, **tabela 5**.

Problem je bil z raztapljanjem nikljeve zlitine, ki vsebuje 5 % Nb. Dodatek H_2SO_4 ni zadoščal, popolno raztopitev vzorca je omogočil dodatek 1 ml HF.

ZAKLJUČEK

Preštudirali smo ločbi jodidov Ag, Bi, Cd, Pb, Se, Sn in Te ter ugotovili, da sta obe ločbi uporabni za vse našteje elemente, medtem ko je za Zn uporabna le TOPO-MIBK ločba. Preverjeni tehniki sta uporabni za analizo tistih elementov sledov v jeklih in superzlitinah, ki so zanimivi za metalurgijo. Odlikuje ju dobra točnost, ponovljivost in odlična občutljivost.

CONCLUSION

In this study it has been shown that the solvent extraction of Ag, Bi, Cd, Pb, Se, Sn, and Te-iodides can be used as with TOPO-MIBK as with TOA-MIBK procedures of separation, only Zn can be separated only with TOPO-MIBK. The proven technics are available for the analysis of steels and superalloys for trace elements of metallurgical interest. The methods offer satisfactory accuracy, good reproducibility, and excellent sensitivity for each element determined.

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