Determination of 22 trace elements in high-purity copper including Se and Te by ETV-ICP OES using SF6, NF3, CF4 and H2 as chemical modifiers

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Determination of 22 trace elements in high-purity copper including Se and Te by ETV-ICP OES using SF_6, NF_3, CF_4 and H_2 as chemical modifiers

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In supplementary work to the one published earlier[1], experiments with SF_6, NF_3, CF_4 and H_2 as new modifier gases for the matrix studied were performed. Our investigations were continued to improve the described analytical method and to achieve additional insights into the mechanism of analyte release. Our new survey is split in two parts. At first fluorinating modifier were used to investigate the behaviour of a variety of trace elements (Ag, Al, As, Au, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Pb, Sb, Se, Si, Sn, Te, Ti, Zn and Zr). Most of them (exceptions Au, Se, Te) could be effectively released from the copper matrix by thermo-halogenation reactions and by partial sub-sample evaporation. Using SF_6 and NF_3 as modifier gases, low limits of quantification (LOQ) were achieved for the 19 well released trace elements (typical ≤ 0.1 mg kg^{-1}). Most elements (exceptions Ag, Mg, Ni) could be calibrated by using aqueous calibration solutions without any sample pretreatment. For the trace determination of Se, Te, Au and a further analytical method of ETV-ICP OES is described in the second part based on thermo-hydrogenation reactions by using a hydrogen/argon mixture as modifier gas. The determination of Se and Te with very high analytical performance (LOQ < 0.1 mg kg^{-1}) can either be carried out in a second analytical step succeeding the halogenation procedure, or the sub-sample is directly treated with H_2 without previous halogenation procedure whereby the sub-sample can either be partially or totally evaporated. In this case some other analytes (Ag, Au, As, Bi, Cd, Fe, Mg, Ni, Pb, Sb, Sn, Zn) can additionally be quantified simultaneously with Se and Te.

Introduction

An increasing demand for high-purity copper in various fields is dominating the market, especially in microelectronics[2] and other fields of modern technology[3-6]. Even low levels of impurities can negatively influence its electrical conductivity and many other important physical properties. Particularly the importance of traces of Se and Te made their determination to the subject of this paper. The ability to produce high-purity copper is directly linked to the availability of sensitive and efficient analytical methods. Different analytical methods were discussed[7] and compared[8] in the past to determine the degree of purity of copper materials including the determination of all traces in a primary copper reference material[9].

Direct solid sampling methods for multi-element determination

In metallurgical production direct and automatable analytical methods are preferred. Already in early times the "arc spectral analysis" was used for copper trace analysis[10-13]. The spectral analysis of pure copper by globule arc technique was summarized by MAASEN[14,15]. Its performance was further developed by different authors[11,16,17]. TYMCHUK[18, 19] reported on the enhancement of emission signals by solid halogenating substances. Different authors reported on a positive analytical effect of using oxidized sub-sample surfaces[20,21]. The globule arc technique combined with modern spectrometers[7] is still in use. With this technique MAHAR[22] et.al. achieved very high analytical performance.

Analytical procedures of copper analysis using spark-OES[23] and X-ray fluorescence spectrometry (XRF)[24,25], respectively, were standardized as European standards, even though their detection power, especially of XRF, is limited. This also applies to glow discharge optical emission spectrometry (GD-OES)[26], but its sensitivity can be improved using the hollow cathode effect[27]. The very sensitive glow discharge mass spectrometry (GD-MS)[28] can be calibrated by synthetic calibration samples[29-32] but needs a high-cost instrumentation. Nuclear analytical methods[33] such as instrumental neutron activation analysis (INAA) or activation analysis with high-energy photons (PAA) as well as XRF with synchrotron radiation (SY-XRF)[34] are specialized and expensive methods mainly restricted to research institutes. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is gaining importance in the metallurgical field [35-39] because of its high sensitivity, but its use for routine bulk analysis of pure metals is currently not the state of the art because its robustness was not widely demonstrated up to now.

Methods with chemical decomposition of the samples

The drawbacks of wet-chemical methods are well known (time need, risk of losses, contamination, etc.). But the preparation of matrix adapted calibration solutions is much easier than the production of appropriate solid calibration samples.

The atomic absorption spectrometry (AAS)[40] is of very high selectivity and high precision, but a sequential mono-elemental method (exception HR-CS AAS). Flame AAS (F-AAS) is very robust, but matrix separation can be necessary[41]. Electro-thermal atomization AAS (ET-AAS) can be used for the trace determination in high-purity copper[42-44]. Inductively coupled plasma optical emission spectrometry (ICP OES) and ICP-MS are mostly accepted analytical methods for the multielement trace determination in solutions of decomposed pure metals. ICP OES was used for pure copper[45,46] also combined with hydride generation technique[47]. The capability of HR-ICP-MS for the multielement trace determination in high purity copper was investigated[35,36, 48,49] and compared with ICP-MS and ICP OES[50,51]. Extremely accurate results were achieved combining isotope dilution technique with ICP-MS (ID ICP-MS)[52-54]. Total reflexion X-ray fluorescence spectrometry (TXRF) was used for trace analysis[87] of high-purity copper in combination with electrolytic removal of the copper matrix.

Basic consideration of ETV-ICP OES method for copper

The globule arc technique and the use of halogenating substances, lead to our idea to investigate the usability of ETV-ICP OES for the analysis of pure copper combined with the application of halogenating gases.
Main advantages of ETV-ICP OES compared to the DC arc techniques are the superior precision and trueness and that chemical modifiers, mostly halocarbons, can be used easily and effectively. Additionally the use of autosamplers of ETV systems is a very important aspect for routine analysis. In the past many different matrices were successfully analyzed by ETV-ICP OES, biological samples[55,56,88,89], soil, sediments[57,90], ceramic materials[58-63] refractory metals[64] and coal[91]. As shown in the first part of our publication to avoid strong matrix load in the ICP plasma only a small part of Cu matrix is evaporated under the optimized conditions (about 0.1 to 0.4 mg of a 20 mg sample). In our first paper we considered effects described in literature [20,21,65,66] of globule arc technique concerning the significant and positive influence of oxygen or of an oxide layer at the sub-sample surface on the analytical performance. The usage of halogenating gases in ETV was described before only for other matrices than copper. With our current work an improved method was developed based on the first satisfying results of our previous investigation[1].

Basic considerations for further developments of our method

The efficient analytical method developed in our previous work[1] based on the application of CHF_3 as modifier gas showed some limitations and problems summarized here. With the development of the new method it was tried to consider or to overcome them:

(1) The necessity to apply a "roasting" (surface oxidizing) procedure as preliminary sample preparation step to guarantee trustable results.
(2) Not all analytes could be calibrated by using dried amounts of calibration solutions, which would be of metrological and practical advantage.
(3) Some elements could not (Se, Te) or not sufficiently (Ag, Mg, Ni) be released from the matrix by halogenation reactions and could therefore not (or only limited) be determined and quantified.

At first, the modifiers SF_6, NF_3 and CF_4 were used alternatively to halocarbons for the first time in ETV-ICP OES. They were studied concerning the items (1) and (2). Subsequently, our investigations were mainly focussed on item (3). H_2 was added in defined concentrations to Ar to release Se and Te from the matrix by thermo hydride forming. In this frame several other analytes were also investigated.

Experimental

Instrumentation and Working Parameters

Instrumentation

The investigations were performed using an IRIS ADVANTAGE ICP-spectrometer (Thermo Fisher Scientific, Waltham, USA) and two ARCOS ICP-spectrometers (SPECTRO A. I. GmbH & Co. KG, Kleve, Germany), one of them used in radial (SOP) and one in axial (EOP) observation of the ICP plasma. The technical parameters of the spectrometers allow time-resolved measurements of line intensities and of the corresponding background intensities.

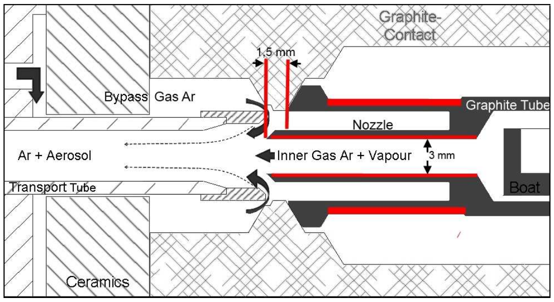


Fig. 1 Schematic detail drawing of the ETV-furnace in the modified design

For sample introduction electrothermal vaporization units (ETV 4050 A, Spectral Systems, Fürstenfeldbruck, Germany) were used. The set-up of the ETV system in details is shown in Fig. 1 of our previous work[1]. For higher amounts of evaporated copper, especially arising with H_2 as modifier, the ETV configuration was modifieded (see Fig. 1, red marked parts) by shortening the outside part (from 3.5 mm to 1.5 mm) and by increasing the inner diameter of the nozzle (from 2 mm to 3 mm) as well as by reducing the wall thickness of the outer graphite tube at the side of the nozzle (from 1.0 mm to 0.6 mm). The changes led to higher temperatures of the graphite tube near the nozzle and thus to higher nozzle temperatures at its end mainly caused by radiation transfer (an increase of 200 °C - 300 °C was measured at the end of the nozzle). The long-term stability of the ETV unit could be increased by twice (up to 60 measurements) and potential depositions resulting from the matrix or from decomposition products (carbon) of the modifier gases dropped by more than half. The temperature control of the furnace was performed by a built-in optical pyrometer. The flow rates for inner-gas, bypass-gas and modifier-gas were mass-flow controlled. The

ETV system was equipped with a 50-fold auto sampler. The synchronization of the ETV system and the spectrometers was realized by a software integrated handshake signal. For drying of aqueous element solutions a drying device (T/IR 250, Spectral Systems, Fürstenfeldbruck, Germany) was used. For all relevant technical data see Table 1.

Table 1: Instrumentation and optimized working parameters

Apparatus	Parameter	SPECTRO ARCOS	IRIS ADVANTAGE
OES	Mounting	Paschen Runge	Echelle
	Focal length / mm	750	381
	Grating / grooves mm^{-1}	2 x 3600. 1 x 1800	60
	Wavelength range / nm	130-770 (first order)	175-1000
	Detector	32 CCD arrays	CID chip
	Number of pixels	32 x 3648	512 x 512
	Dispersion / nm pixel^{-1}	at 200 nm 0.0035	130 to 340 nm 0.0030
	Plasma observation	a) radial (SOP) b) axial (EOP) *)	only axial used
ICP	ICP Plasma RF-power / W	1500	1150
	Coolant gas flow rate / L min^{-1}	15	14
	Auxiliary gas flow rate / L min^{-1}	1.3	1
	Aerosol gas flow rate / L min^{-1}	0.55	0.52
	Inner diameter of alumina injector tube / mm	1.5	1.5
ETV	Length of PTFE transport tube / mm	ca. 400	ca. 450
	Inner diameter of transport tube / mm	4	4
	Inner-gas flow rate / L min^{-1}	0.15	0.14
	Bypass gas flow rate / L min^{-1}	0.4	0.38
	Modifier gas flow / mL min^{-1}		
	for SF_6	1.2 (0.8 - 1.2)^{x}	1.2 (0.8 - 1.2)^{x}
	for NF_3	2.7 (2.5 - 3.0)^{x}	2.7 (2.5 - 3.0)^{x}
	for CF_4	2.4 (not determined)^{x}	2.4 (not determined)^{x}
	for H_2/Ar mixture (0-30vol.% H_2) (optimum 28 vol.%) **	see inner-gas flow rate	see inner-gas flow rate
	Shape of graphite sample boat	Modified globule type boat as shown in Figure 2b of our previous work[1]	

*) Investigations were carried out by using two different ARCOS spectrometers only differing in - a) radial observation (side on plasma SOP) or b) axial observation (end on plasma EOP); ** relevant only for the second part of this publication; ()^{x} determined optimum range

Table 2: The five different ETV temperature programs used: TP-stand, TP-ramp, TP-plat, TP-part and TP-tot

	T-program standard (TP-stand)		T- program const. Ramp (TP-ramp)		T- program plateau (TP-plat)		T- program part. evap. (TP-part)		T- program tot. evap. (TP-tot)	
step	Time / s	Temp /°C	Time / s	Temp / °C	Time / s	Temp / °C	Time / s	Temp / °C	Time / s	Temp / °C
start	0	RT*)	0	RT*)	0	RT*)	0	RT*)	0	RT*)
ramp 1	13	RT→480	15	RT→400	10	RT→650	10	RT→500	10	RT→700
hold 1	12	480	10	400	15	650	10	500	0	700
ramp 2	7	480→1200	rt**)	400→ET**)	3	650→1200	10	500→1200	10	700→1100
hold 2	0	1200	10	ET**)	27	1200	0	1200	0	1100
ramp 3	8	1200→1500	20	cooling	20	cooling	10	1200→1750	10	1100→1600
hold 3	0	1500					0	1750	0	1600
ramp 4	10	1000→1630					2	1750→2250	3	1600→2400
hold 4	0	1630					0	2250	0	2400
ramp 5	20	cooling					4	2250→2300	27	2400→2600
hold 5							0	2300	0	2600
ramp 6							20	cooling	20	cooling

*) RT = room temperature; **) ramp time (rt) and end temperature (ET) depending on experiment (e.g. rt = 140 s and ET = 2300 °C)

Working parameters

The ETV-ICP OES conditions of the used spectrometers are also given in Table 1. The temperature programs used are summarized in Table 2. The spectral lines used are specified in according tables and figures. The ICP OES parameters used were in accordance with the recommendations of the manufacturers for analysis of dry aerosols. The sum of inner gas and bypass gas flow-rate corresponded to the recommended aerosol-gas flow-rates.

Chemicals and Materials

Argon with purity of 4N (SWF, Friedrichshafen, Germany) was used as working gas for ETV and ICP. The chemical reaction gases added to the inner gas stream of argon as modifier gases were SF_6, NF_3, CF_4 (ABCR, Karlsruhe, Germany) and H_2 (SWF, Friedrichshafen, Germany) with a purity of 4N for H_2; for SF_6, NF_3 and CF_4 a purity of better 99.5 % was warranted.

All reagents were of high purity. HNO_3 (Merck, Darmstadt, Germany) was distilled under sub-boiling conditions in a PFA sub-boiling system. Ultrapure water (18.2 MΩ) was obtained from a Milli-Q-Plus system (Millipore, Schwalbach, Germany). The aqueous stock solutions were prepared from pure metals (Alfa Johnson Matthey, Karlsruhe, Germany) or from materials of the National Primary Standards for Elemental Analysis certified by BAM[16]. To stabilize the final calibration solutions, 2 mL sub-boiled HNO_3 per 100 mL were added.

As pure copper materials six certified reference materials BAM-M381, BAM-M382, ERM®-EB383, ERM®-EB384, ERM®-EB385, and BCR 074 were used. All information and mass fractions of impurities of CRMs used are available from their certificates[72,73]. The sub-sample masses of CRMs were chosen in a range of about 5 mg – 40 mg, according to their analyte mass fractions and depending on the analytical technique used.

Results and Discussion

General Remarks

To compare signal intensities of spectral lines between copper CRMs and aqueous element solutions the different absolute analyte mass of their sub-samples was taken into account via peak area of background corrected transient signals (intensities versus time curves). These signal intensities are assumed to correspond with the release behaviour of the analytes from the copper sub-samples. For better visualization in the figures only a representative selection of elements is shown. Therefore the number of analytes and their selection are different in the different figures.

The time interval of measuring was determined and, if necessary individually fixed for each analyte starting about 1 s before first appearance and ending about 1 s after disappearing of spectral line intensity of the respective spectral line. Thus the optimum signal to background ratios (SBRs) could be achieved.

All time resolved measurements were calculated using specific excel-sheets basing on ASCII raw data recorded by the spectrometer.

Halogenating modifier gases

Optimization of the modifier gas flows

The modifier gas flows were optimized based on experiences[1] with CCl_2F_2 and CHF_3. Optimization criterion was the dimension of the measured net intensities of spectral lines based on measurements in an interval of 0.1 – 4.0 mL min^{-1}. For gas flows used in our measurements and for determined optimum ranges see Tab. 1.

Modifier gases and oxidation states of sub-sample surfaces

To investigate the influence of the halogenating modifiers SF_6, NF_3, or CF_4 on the determination of impurities in pure copper and on the copper matrix itself experiments with and without modifier were made. The investigations were carried out using the CRMs ERM®-EB385 and ERM®-EB384 and additionally dried aqueous element solutions. The dynamics of the release (release behaviour) of the analytes were characterized by their time resolved analytical signals.

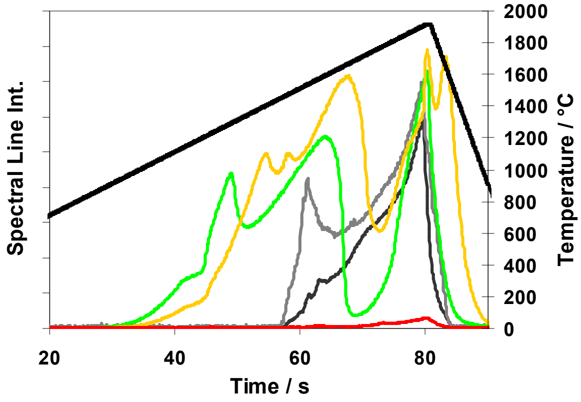


Fig. 2 Spectral line intensities of copper using CRM ERM®-EB385 (20 mg ± 1 mg) with modifier gases SF_6 ▬, NF_3 ▬, CF_4 ▬, CF_4 sub-sample oxidized (roasted) ▬ and without modifier gas ▬; temperature T versus time ▬, according to the temperature program "TP-ramp" of Tab. 2, gas flow rates see Tab. 1

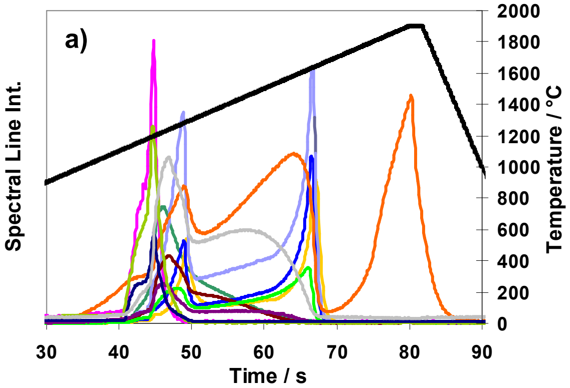
Fig. 2 gives an impression of the different release of copper matrix material (ca. 0.2 mg to 0.4 mg) from sub-samples (ca 20 mg). From observed release behaviour it can be concluded that SF_6 and NF_3 are decomposed in Ar atmosphere generating reactive fluorine gas and/or other reactive decomposition products at much lower temperatures than CF_4. This holds for CF_4 independent from the surface state of the sub-samples (unoxidized or oxidized state after “roasting” at 400 °C in air for 30 min in a muffle furnace). However the signal of the “roasted” sub-sample achieves clearly higher values than the one arising from the unprepared sub-sample, whereas a comparable significant effect wasn't found for SF_6 and NF_3. This may be a first declaration for different release behaviour of roasted and not roasted copper sample using CF_4. The differences between the copper signals determined for the modifiers SF_6 and NF_3, respectively, could be explained by the different reactivity of sulphur and of nitrogen. The very low copper signal using no modifier is a clear evidence for the reactivity of the modifiers with the matrix and therefore also for most of the analytes having similar chemical reactivity with halogens. From this fact the necessity of using the modifiers in the analytical process can be concluded. The reproducible significant intensity drop-off measured for SF_6 and NF_3 between about 1500°C to 1600°C were not a consequence of a special boiling behaviour of the sample material but rather of chemical reactions between the modifier constituents and the copper material depending on the reaction temperature. As observed by additional measurements this drop-off is independent of purity grade of copper samples.

In Fig. 3 the release behaviour of 11 analytes as well as of Cu measured at sub-samples of the CRM ERM®-EB385 in unoxidized state of surface are depicted exemplarily using NF_3 as modifier gases.

As shown in Fig. 3 the analytes itself can be divided in three groups concerning their release behaviour, using NF_3 as modifier (nearly same analyte behaviour can be stated for SF_6):

- First group: As, Bi, P, Sb, Si, Sn, Ti, Zr
- Second group: Cd, Co, Cr, Mn, Ni
- Third group: Al, Fe, Pb, Zn
- Not assignable: Ag, Mg

The release behaviour of analytes using CF_4 shows only one group like first group of NF_3 or SF_6 beginning with the appearance of the copper signal, with a very narrow temperature range at which the signals start or reach their peak maxima. This can be explained by the significantly delayed reaction of CF_4 with copper, – see Fig. 2.



Figs. 3 Spectral line intensities of Al —, As —, Cd —, Co —, Cr —, Fe —, Ni —, Pb —, Sn —, Ti — and Zn — as well as of Cu — using CRM ERM$^{®-}$ EB385 and NF_3 as modifier gase; temperature T versus time —, according to temperature program "TP-ramp" of Table 2.

To study the effect of the oxidation step of sub-sample surfaces and the possibility to calibrate with solutions, the intensities of 19 analytes (Ag, Al, As, Bi, Cd, Co, Cr, Fe., Mg, Mn, Ni, P, Pb, Sb, Si, Sn, Ti, Zn, Zr) were measured using the three modifiers and applying the temperature program "T-stand" (Table 2) to roasted (oxidized) and not roasted (unoxidized) sub-samples of CRM ERM®-EB385 as well as to dried sub-samples of aqueous element solutions. Excluding the analytes Ag, Mg, Ni, Sb which showed “critical” results, the results of comparisons of the mean values (n = 4) of intensities of the remaining 15 analytes can be summarized:

- SF_6 and NF_3 used as modifier:

The expected trueness of results of calibration using aqueous solutions will be high, because the relative deviation of compared intensities of solid CRM’s and of aqueous sub-samples was < 15% and in most cases even < 5 % (up to 73% of all elements). For aqueous calibration the quality of results would not (SF_6) or not essentially (NF_3) be improved by a preceding roasting procedure. The most important conclusion was that for all analytes trustable results are to expect when copper CRMs will be used for calibration independent from the oxidation state. This can be concluded, because the relative deviation of intensities measured at roasted and not roasted sub-samples, respectively, was < 15 rel %, in most cases even < 10 % (SF_6, 66% of all) or < 5 % (NF_3, 73% of all). In other words: The oxidation state of the surface of sub-samples has no influence of calibration with CRMs.

- CF_4 used as modifier:

Among the three investigated halogenating modifiers CF_4 was the least appropriate one, as well in the case of aqueous calibration as of calibration based on solid copper CRMs Compared to CHF_3 (found to be the best modifier in our former publication[1]), the performance of CF_4 was worse, accordingly CF_4 was not included into all our subsequent experiments.

Temperature program and analyte release

To find the optimal release of the analytes from the copper sub-samples the spectral line intensities were determined using temperature program TP-plat and TP-ramp to get an overview of the release behaviour of Ag, Al, As, Bi, Cd, Co, Cr, Fe, Mg, Mn Ni, P, Pb, Sb, Si, Sn, Ti, Zn and Zr and of the copper matrix. For program TP-plat the temperature which led to the highest signal intensities was determined for each analyte as the plateau temperature of hold 2 that corresponded with the maximum integrated intensity of the transient signals. Steps of 50 °C were used in an interval from 1000 °C to 1700 °C. For program TP-ramp this temperature was determined for each analyte that corresponded with maximum peak intensity values of the transient signals considering the second peak in cases double peaks were observed.

A comparison of the boiling points of fluoride compounds as well as of the pure elements of all analytes with their observed maximum release temperatures led to the following summary of results:

- Most analytes including Cu (exceptions are Cd, Mg, Zn) have boiling points of their fluorides at lower temperatures than those of the elements itself.
- The boiling points of most elements (exceptions are As, Bi, Cd, Mg, P, Zn) are higher than the highest heating temperature of the optimized temperature program "TP-stand" (1650 °C).
- The maximum release temperatures of all analytes with boiling points > 1100 °C (≈ melting point of Cu) are below their boiling points.
- The maximum release temperatures of all analytes with boiling points < 1100 °C (As, Cd, Mg, P, Zn) are above their boiling points.

The facts can be interpreted as a clear indication that from the moment when the matrix liquefies/melts, chemical reactions especially halogenation reactions dominate the release behaviour of most elements. Based on these results the standard temperature program “TP-stand” as depicted in Fig. 4 was developed which can be used for both modifiers SF_6 and NF_3 and which is leading to very acceptable analytical results concerning trueness, precision and limits of quantification. From Fig. 4 it can be concluded that analytes of different release behavior can be released from the samples in a way that all analyte signals drop to the baseline before the end of the program time. There are differences between the time dependent spectral line intensities of the different analytes as also described in connection with Fig. 3. Nearly the same release behaviour of analytes as shown in Fig. 4 using SF_6, was found for NF_3.

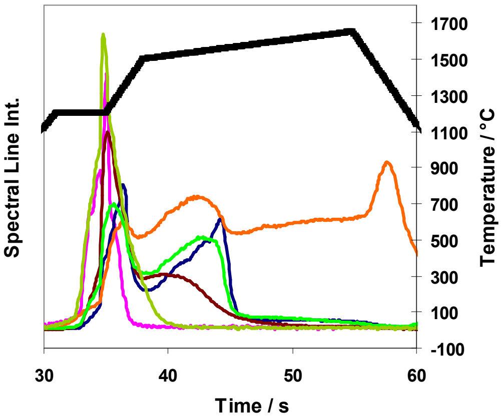


Fig. 4 Spectral line intensities of As —, Co —, Cu —, Fe —, Ni — and Sn —, released from sub-samples of copper CRM ERM®-EB384 (20 mg ± 1 mg). Modifier gas: SF_6, (gas-flow rate see Tab 1) and temperature *T* versus time — using "TP-stand" of Table 2.

Calibration

Working conditions are listed in Tables 1 and 2. The temperature program "TP-stand" was used for all following results. Two different calibration methods were used and compared, one of them using aqueous calibration solutions and the other using reference materials with certified mass fractions of analytes. Some examples of these investigations are given in Fig. 5 in the form of linear calibration functions.

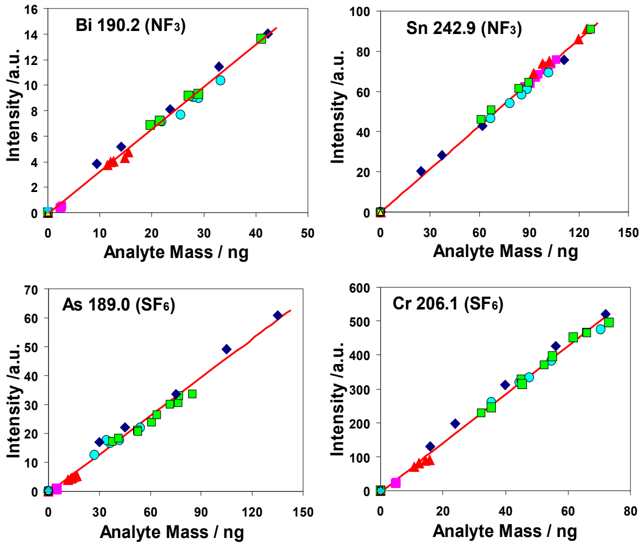


Fig. 5 Examples of calibration functions based on different volumes of the aqueous calibration solution cuAD556/7 (♦) as well as on different sub-sample masses of the copper CRMs BAM-M381 (■), BAM-M383 (▲), ERM®-EB384 (●), ERM®-EB385 (■); blank (= empty sample boats) (▲); — common linear regression line

The common linear regression lines of different analytes are depicted based on measurements of copper CRMs as well as of dried aqueous calibration solutions. As a result of statistical tests[74,75], the statistical equivalence of both calibration methods could be stated for the elements Al, As, Bi, Cd, Co, Cr, Fe, Mn, P, Pb, Sb, Si, Sn, Ti, Zn and Zr. This was an evidence of the high trueness of results which can be achieved for these elements using a calibration with aqueous sub-samples. For Ag, Mg and Ni the calibration functions differed significantly. However, for these analytes a calibration with matrix reference materials led to results of very satisfying trueness and reproducibility.

The coefficients of determination (R^2) based on the linear calibration functions were calculated for all investigated elements, except Ag. For NF_3 as well as SF_6 15 of 18 analytes have R^2 values higher than 0.99 with the exception of Cd, Sb and Ti (for NF_3) and of Mg. Ni and Zr (for SF_6), though these outlying values were only slightly smaller than 0.99. This result was assessed as an indication of a sufficient grade of linearity of the calibration functions and of a satisfying statistical compatibility of the calibration points derived from different sources of calibration materials namely from different CRMs as well as from an aqueous calibration solution. Exceptions from the statistical homogeneity of results of different calibration modes were the results of analytes Mg and Ni for which satisfying calibration could only be achieved based on calibration with copper CRMs.

Limits of quantification (LOQs)

Table 3: LOQs for sub-sample mass of 20 mg determined for SF_6 and NF_3 as modifier gases using different spectrometers and observation conditions of ICP (see Table 1) ; "—" = not measured; "- -" = contaminated blank samples

Limit of quantification (LOQ) calculated by 9s-crit.						
device	Arcos SOP	Arcos	Arcos SOP	device	IRIS Adv.	IRIS Adv.
Modifier	SF_6	SF_6	NF_3	Modifier	SF_6	NF_3
Plasma	radial	axial	radial	Plasma	axial	axial
Element	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	Element	mg kg^{-1}	mg kg^{-1}
Ag 338.2	0.29	0.08	0.10	—	—	—
Al 308.2	0.07	0.15	0.09	Al 237.3	0.05	0.21
As 189.0	0.07	0.05	0.08	As189.0	0.03	0.03
Bi 190.2	0.24	0.13	0.36	Bi 190.2	0.03	0.05
Cd 226.5	0.03	0.04	0.03	Cd 226.5	0.01	0.01
Co 230.7	0.05	0.07	0.01	Co 230.7	0.02	0.01
Cr 267.7	0.04	0.04	0.01	Cr 266.6	0.02	0.03
Fe 241.3	0.08	0.13	0.07	Fe 233.2	0.36	0.07
Mg 279.0	0.10	0.09	0.12	Mg202.5	0.44	0.29
Mn 293.3	0.16	- -	0.06	Mn191.5	0.04	0.06
Ni 231.6	0.11	0.14	0.09	Ni 232.0	0.26	0.31
P 178.2	0.38	—	0.46	P 178.2	0.11	0.13
Pb 168.2	0.12	0.04	0.14	Pb 261.4	0.11	0.06
Sb 206.8	0.53	0.13	0.35	Sb 206.8	0.16	0.07
Si 288.1*	0.08	—	0.21	Si 288.1*	—	—
Sn 189.9	0.05	0.04	0.07	Sn 189.9	- -	0.02
Ti 316.2	0.02	0.06	0.07	Ti 252.5	0.14	0.04
Zn 334.5	0.57	0.41	0.43	Zn 206.2	0.03	0.02
Zr 273.4	0.06	—	0.02	—	—	—

*(Si signals were not calculateded in most cases because of high memory values in the entire systems used coming from matrices of type SiX analysed routinely before)

The limits of quantification (LOQs) listed in Table 3 were calculated by the 9s-criterion[76] using the standard deviations obtained with purified copper blank samples (10 replicate measurements) and using the slopes of the linear calibration functions. Taking into account that results of Table 3 were coming from different spectrometer types, different wavelengths and/or types of plasma observation, differences of a factor of up to 3 (and even of a factor of up to 5 for LOQs < 0.1 mg kg^{-1}) should be considered as not significant. Taking these facts into account, the following conclusions were drawn:

- All determined LOQ values are in the sub-mg kg^{-1} region, independent of spectrometer type and kind of plasma observation.
- In case of SF_6 two different kinds of plasma observation were compared. Only for Ag, Bi, Pb, Sb a significant increase of sensitivity could be found for axial viewing.
- A relatively high number of different LOQ's were found when in case of SF_6 results were compared coming from different types of spectrometers (Arcos, Iris) both using axial plasma observation.

It can be concluded for most analytes that very similar LOQs were achieved independent from the modifier used (SF_6 or NF_3) if the same kind of instrumentation was used for measurement.

Trueness of results

The analytical results for CRM ERM®-EB384 obtained using the optimized method and two different calibration strategies are shown in Table 4 (NF_3 and SF_6 as modifiers). The comparison of the measured values with the certified values was based on calculated "RD" values being absolute values of relative differences between both corresponding mass fractions and expressed in rel % . These relative differences of certified and measured mass fractions (RD values) are a measure of the quality of the recovery rate of the measurements. They were marked grey when they exceeded the tolerable value of 15 rel %. As it can be seen from the tables, the optimized method allows a trustable calibration for all investigated elements using copper CRMs for calibration insofar as this value of 15 rel %. was only slightly exceeded in one case (for Ni with SF_6 modifier). This result is in very good agreement with the results concerning our investigations of the influence of the surface oxidation state of the samples using SF_6 or NF_3. The results of both investigations confirm the conclusion that the calibration with copper CRMs will lead to trustable results of high trueness.

Table 4: Analytical results of CRM ERM®-EB384 using NF_3 and SF_6 as modifier and calibrations based on dried aliquots of the aqueous calibration solution as well as on copper CRMs BAM M381, ERM®-EB383 and ERM®-EB385. m = mean, s = standard deviation (n=5), RSD = relative standard deviation, Spectrometer used: Iris advantage (axial observation).

sample ERM®-EB384	certified values of ERM®-EB384	**calibration using NF_3-Modifier**								**calibration using SF_6-Modifier**							
		dried aqueous calibration solution				Cu CRMs				dried aqueous calibration solution				Cu CRMs			
Element λ / nm	cert. val. U (k=2) /mg kg^{-1} /mg kg^{-1}	m /mg kg^{-1}	s /mg kg^{-1}	RSD /rel%	RD /rel%	m /mg kg^{-1}	s /mg kg^{-1}	RSD /rel%	RD /rel%	m /mg kg^{-1}	s /mg kg^{-1}	RSD /rel%	RD /rel%	m /mg kg^{-1}	s /mg kg^{-1}	RSD /rel%	RD /rel%
Al 257.5	13.0 ± 0,8	13.1	0.3	2.4	0.4	12.7	0.3	2.1	2.2	12.7	0.3	2.1	2.1	12.7	0.3	2.1	2.7
As 189.0	5.0 ± 0,4	5.0	0.1	1.6	0.3	5.7	0.1	1.7	13.8	5.6	0.4	7.7	11.7	5.6	0.0	0.5	11.1
Bi 190.2	3.34 ± 0,22	3.32	0.24	7.1	0.5	3.58	0.07	2.0	7.3	3.31	0.05	1.6	0.8	3.19	0.03	0.9	4.5
Cd 226.5	3.95 ± 0,09	4.77	0.09	1.9	20.7	4.01	0.09	2.2	1.4	4.22	0.09	2.1	6.7	4.02	0.11	2.6	1.7
Co 228.6	3.88 ± 0,16	3.49	0.05	1.5	10.2	3.83	0.06	1.6	1.4	3.34	0.12	3.6	13.8	4.01	0.15	3.6	3.3
Cr 206.1	6.53 ± 0,21	6.10	0.14	2.3	6.6	6.57	0.15	2.3	0.6	6.55	0.15	2.3	0.3	6.31	0.19	3.0	3.4
Fe 216.6	32.8 ± 1,9	34.3	0.1	0.4	4.5	31.8	0.1	0.4	3.1	29.4	0.4	1.3	10.5	32.7	0.4	1.3	0.4
Mg 202.5	14.6 ± 0,5	9.8	0.5	5.3	32.7	15.2	0.8	4.9	3.8	7.4	0.6	7.4	49.4	16.8	2.6	15.4	15.0
Mn 191.5	6.88 ± 0,15	7.18	0.12	1.7	4.3	7.01	0.12	1.8	1.8	6.85	0.17	2.4	0.5	6.84	0.17	2.5	0.6
Ni 232.0	5.7 ± 0,4	3.8	0.3	7.4	33.3	6.0	0.5	8.8	5.3	3.1	0.8	25.2	45.1	4.8	1.3	27.9	15.6
P 185.9	–	0.4	0.1	14.1	–	0.2	0.0	12.6	–	0.7	0.1	21.4	–	0.5	0.1	19.3	–
Pb 261.4	5.7 ± 0,5	6.2	0.1	0.9	7.8	5.7	0.1	1.1	0.4	5.4	0.1	2.6	5.6	6.2	0.2	2.8	8.9
Sb 206.8	12.0 ± 0,4	17.6	0.4	2.0	46.7	12.2	0.2	2.0	1.9	19.1	1.4	7.1	59.1	12.9	0.6	4.8	7.5
Sn 189.9	(10.2 ± 0,9)	10.8	0.1	1.3	6.0	9.9	0.2	1.6	3.1	10.2	0.3	3.3	0.1	10.3	0.3	3.2	1.4
Ti 190.8	(2.1 ± 0,23)	2.2	0.3	13.0	5.8	1.9	0.1	5.2	11.4	2.1	0.1	2.4	0.4	1.9	0.0	2.3	8.0
Zn 206.2	(12.7 ± 2,1)	13.2	0.3	2.1	4.2	13.7	0.2	1.4	8.1	13.4	0.7	5.2	5.2	13.0	0.8	6.3	2.5
Zr 257.1	(< 9)	3.7	0.1	3.0	–	4.1	0.4	9.0	–	3.1	0.3	8.0	–	2.7	0.2	8.0	–

– = not certified; () = indicative values in the CRM certificate, m = mean integrated net intensity values of 5 parallel measurements, s = standard deviation based on the 5 parallel measurements.

Some results based on calibration with aqueous calibration solutions are different from the results based on copper CRMs insofar as in this case the value of 15 rel % was exceeded by RDs of several elements (for Cd, Mg, Ni and Sb with NF_3 modifier and for Mg, Ni and Sb with SF_6 modifier). For all the other analytes the deviation of the measured values (based on a calibration with solutions) from the certified values was very (partly extremely) low (relative deviation of measured from certified values RD < 15 rel % or even < 1 rel %), indicating that for most elements very trustable results based on calibration with aqueous solutions are achievable, too. Summarizing it can be stated that

- The calibration based on copper CRMs will lead to results of high trueness for practically all analytes under investigation and independent of the kind of modifier gas used (NF_3 or SF_6, respectively) or the oxidation state of sub-sample surfaces.
- The calibration based on aqueous solutions will lead to very trustable results for most analytes. Intolerable large deviations of measured from true values of mass fractions were only determined in case of SF_6 as modifier for three elements and in case of NF_3 as modifier for four elements (out of 15).

Precision of results

From Table 4 RSD values can be assessed in case of NF_3 and SF_6 used as modifiers. These values are a numeric expression of the precision of a measurement method. Only eight of the 68 overall measured RSD values (each of them 5 parallel measurements) are exceeding the 10 % value. The number of RSD values exceeding the 10 % level is also a consequence of the relatively low mass fractions of analytes in CRM ERM®-EB384. Comparable results achieved by our investigations on the influence of the surface oxidation state of the samples using SF_6 or NF_3 for a CRM with higher element concentrations (ERM®-EB385) were significantly better.

Manageability of the method

The calibration is very easy and flexible, for example by using only one CRM as calibration material but different masses of sub-samples or by calibrating with different calibration materials of copper. The masses of the solid sub-samples can be in the range of a few mg up to about 40 mg. This can always be applied if the same sub-samples are not additionally intended to be used subsequently for the determination of Se, and Te, as done in the second step of Method M1 (see below). The shape of the sub-samples has no influence on the analytical performance because they all melt to a globule before the actual analytical processes will start. With copper CRMs used for calibration and with SF_6 or NF_3 as modifier gas a defined oxidation step of surfaces of sub-samples is no longer necessary in opposite to the situation when our previously described method[1] would be used. The developed method is fast, requiring only two minutes for one single measurement.

Hydrogen / Argon modifier gas mix

General remarks

As shown before fluorine containing modifiers do not work for Se and Te, what might be essentially caused by their chemical form in the material such as selenides or tellurides, respectively. An visible release (or transport) of Se and Te did not occur at relatively low reaction temperatures as used in our previous investigations. At significantly higher temperatures up to the total evaporation of the sub-samples, applied in combination with halogenating modifiers or without any modifier, Se and Te emission signals were observed. However, their time resolved signals were parallel to those of copper, apparently only in proportion to the evaporated copper, and their evaluation did not allow any trustable quantification.

Methods for determination of Se and Te in pure copper

Many analytical methods described in the introduction of this paper include the determination of Se and Te. In[8] limits of detection (LOD, 3s-criterion) were given for up to 22 trace elements, among them Se and Te. In[29] for GD-MS analysis of high-purity copper estimated levels of LOQ values (9s-criterion, /µg kg^{-1}) of 57 analytes were specified, among them for Au (10-50), Te (100-200) and Se (200-1000). By using globule arc technique with a modern equipment described in[22], limits of detection were determined also for Se (0.4 mg kg^{-1}) and Te (0.1 mg kg^{-1}). In different investigations ET AAS was used to determine Se and Te in pure copper by enrichment procedures based on co-precipitation[77-80], LOD values down to sub-mg kg^{-1} level were achieved. Hydride generation AAS (HG AAS) is used to determine Se and Te by chemical hydride forming[81], but several procedures include additional chemical[82] or electrolytic[83] removal of copper matrix. Also ICP OES was combined with hydride generation steps for determination of hydride forming elements[84-86] in pure copper.

Basic considerations

Based on the idea of hydride generation hydrogen was used as reaction gas in ETV-ICP OES to determine Se and Te by thermo-hydrogenation. Additionally the behaviour of all other trace elements, including Ag, Au, Mg, and Ni, was investigated. Three different ways how to analyze pure copper samples considering especially Se and Te are shortly described in the following:

- Method 1 (M1) – Determination of all relevant analytes in two steps

First step: halogenation including partial evaporation (0.1 – 0.3 mg of 20 mg) of a Cu sub-sample and determination of relevant analytes as described in the first part of this paper.
Second step: treatment with hydrogen including partial evaporation (3 – 4 mg) of the same Cu sub-sample for determination of Se, Te and Ag (> 90 % of Ag remain in the sub-sample) by using an Ar/ H_2 mixture at high temperatures (short temperature peak > 2200 °C).

- Method 2 (M 2) – Determination of Bi, Se, Te and several other analytes in one single step by partial evaporation

Single step: treatment with hydrogen including partial evaporation (3 – 4 mg of 20 mg) of a Cu sub-sample by using an Ar/ H_2 mixture at high temperatures (short temperature peak > 2200 °C) and determination of Bi, Se and Te and several other analytes which are also released from the copper sub-sample.

- Method 3 (M 3) – Determination of Bi, Se, Te and several other analytes in one single step by total evaporation

Single step: treatment with hydrogen including total evaporation of a Cu sub-sample (2 - 5 mg) at high temperatures (up to 2500 °C) and determination of Bi, Se and Te and some other analytes which are also quantitatively released.

In the following basic investigations with H_2 as reaction gas the Methods M2 and M3 were preferably considered. The signal intensities in all following figures are averages of at least three replicated measurements.

Basic parameters of H_2 method

H_2 - Ar ratio in the inner gas flow

Note: The temperature conditions of TP part (see Tab 2) or similar were used for successive investigations.
As first investigations to study the dependence of the spectral line intensities of the elements released by hydrogenation on the hydrogen concentration in the inner gas flow, copper CRM ERM®-

EB385 was used. The results for 11 selected analytes plus copper are depicted in Fig. 6 depending on increasing hydrogen concentrations in inner Argon flow.

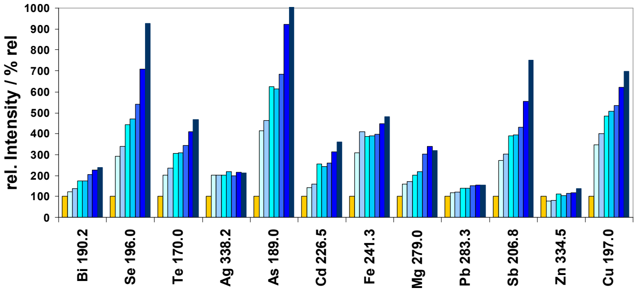


Fig. 6 Spectral line intensities, normalized to 0 % H_2, of 11 analytes and of Cu measured using CRM ERM®-EB385 (sub-sample mass = 20 mg ±1 mg) depending on different concentrations of H_2 modifier in the inner Ar gas flow of the ETV (total inner gas flow rate 150 mL min^{-1}). Investigated hydrogen concentrations: 🟨 0 %, ⬜ 4 %, ■ 7.5 %, ■ 11.2 %, ■ 15 %, ■ 19.2 %, ■ 25 %, ■ 32 %.

It can be concluded from Fig. 6 that the signals of almost all selected hydride forming elements (Bi, Se, Te, As, Sb, Sn) are significantly increased by increasing the concentration of the hydrogen modifier gas. This fact can only be interpreted by improved release and transport efficiencies of formed analyte hydrides. The intensities of some of the other elements (Cd, Fe, Mg) and of copper matrix are also increased, whereas the intensities of all other elements (Ag, Pb, Zn) are not much changed. Additional investigations were restricted to Bi, Se, Te (as most important analytes). Intensities as well as mass losses were clearly increased with increasing H_2 concentration; however the increase of the intensities was larger than the increase of the mass loss, especially for Se, Te and Cu. It could be concluded that these three trace elements as well as the copper matrix react with hydrogen by forming their hydrides. Even for the matrix Cu the increase of intensity is higher than the increase of sub-sample mass loss. One explanation could be that the transport efficiency of the copper atoms in case of measurements without modifier or with low concentrations of modifier, is lower than with higher concentrations because copper hydride molecules are formed in a progressive rate.

Optimization of the releasing temperature

As optimum release temperature for the different analyte elements by using CRM ERM®-EB385 and H_2 as modifier gas an optimal temperature of TP-part (see Table 2) of about 2200°C ± 50 °C was identified. At higher temperatures lower intensities were observed for most elements, probably resulting from change of plasma conditions according to higher concentrations of copper atoms in the plasma (plasma loading).

Gas flow rate of inner gas flow

To investigate the influence of the flow rate of the inner gas on the line intensities of the analytes the flow rate of the inner gas flow was varied from 90 mL min^{-1} to 210 mL min^{-1}. The concentration of the H_2 gas in the inner gas flow was adjusted to 29 % while the flow rate of the bypass gas was 400 mL min^{-1} for all measurements. The maximum intensities of the analyte elements were observed with inner gas flow rates of 120 – 170 mL min^{-1}. From this result a compromised optimum inner gas flow rate of 150 mL min^{-1} by using a bypass gas flow rate of 400 mL min^{-1} was defined as constant parameter of Methods M2, M1 (second step) and M3.

Sub-sample mass

The dependence of measured spectral line intensities on the sub-sample mass was investigated using Method M2. It was found that the intensities of all analytes normalized to the corresponding analyte mass were not constant, but decreasing with increasing sub-sample masses. The different extent of this effect is demonstrated in Fig. 7 for Bi, Se and Te. Among all analytes (as listed in Table. 5 or 6) this effect was most distinct for Se and smallest for Mg.

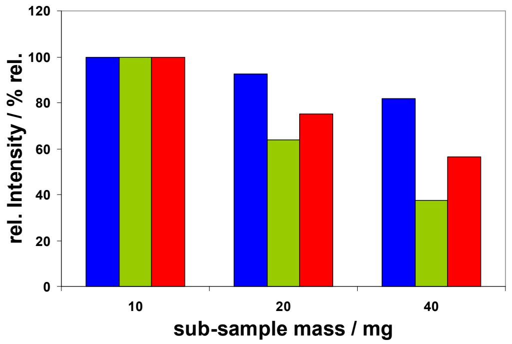


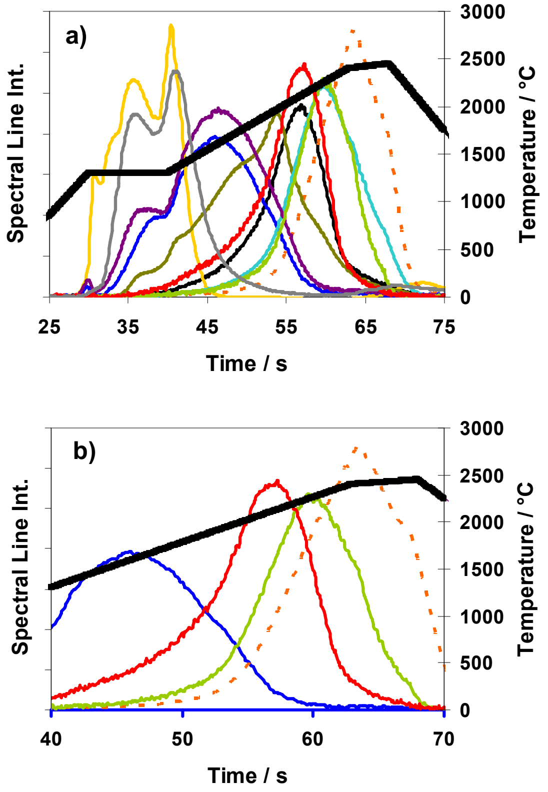
Fig. 7 Spectral line intensities, normalized to 10 mg Cu, of 🟦 Bi, 🟩 Se, and 🟥 Te depending on different sub-sample masses of 10 mg, 20 mg and 40 mg. (H_2 concentration 20 %, inner gas flow rate 150 mL min^{-1}, T- program TP-part).

The decrease of the normalized intensities with increasing sub-sample masses would lead to curved calibration functions if these would be based on different masses. To achieve straight calibration functions sub-sample masses of about 20 mg ± 1 mg were recommended for Method M2. The same holds for Method M1, if not only its first part is intended to be used. The observed effect can be explained by the fact, that the mass of an analyte in a sub-sample is proportional to the sub-sample mass, and therefore in case of a globular sub-sample (with a radius of r) proportional to r^3, whereas the surface of this globular sub-sample is proportional to r^2. Hence the relation between the surface area which is available for hydrogenation reactions and the analyte mass in the sub-sample ready to move to and to react with hydrogen at this surface becomes step by step smaller with increasing sub-sample masses. This fact seems to be the main reason for the observed effect. An increasing effect of plasma loading can probably be excluded because the evaporated mass of copper can not be directly correlated to the sub-sample mass: 10 (4.5) mg, 20 (4.8) mg and 40 (5.3) mg, evaporated mass of Cu in brackets. For Method M3 sub-sample masses of 3-5 mg were fixed to come to reproducible evaporation times and to minimize potentially caused depositions in the ETV system. All subsequent studies with this method showed no significant dependencies of the results on sub-sample masses within this small range of weighing.

Checking calibration by dried element solutions

Intensities of different analytes (Ag, Bi, Cd, Mg, Pb, Se, Te, Sn) coming from dried sub-samples of a calibration solution were compared with intensities from sub-samples of copper CRM ERM®-EB385. It could be concluded that in case of both methods (M2 and M3) based on hydrogenation reactions the quantification via dried aqueous solutions is limited and would only allow semi-quantitative analyses.

Release behaviour of analytes using optimized programs



Figs. 8a and 8b Spectral line intensities (signal-addition of 3 sub-samples) with H_2 as modifier (conc. 29 %; inner gas flow rate 150 mL min^{-1}) of Ag ▬, Bi ▬,Cd ▬, Cu ▪ ▪ ▪, Mg ▬, Mn ▬, Pb ▬, Se ▬, Te ▬, and Zn ▬, using CRM ERM®-EB385, - and temperature *T* ▬ versus time (Temp. program "TP-ramp$_{spez}$", see temperature-curve progression). Fig. 8b shows as a magnified detail of Fig. 8a selected scans of Bi, Cu, Se and Te.

In Fig. 8 the time resolved line intensities of 10 selected elements including Cu are depicted together with the time function of ETV temperature for partial evaporation of sub-sample (Method M2). This temperature program TP-ramp$_{spez}$ represents a mix of different temperature program styles. It was modified to receive more distinct intensity peaks. From Fig 8a one can conclude that all maxima of release of the analytes lie at lower temperatures than the maximum of Cu which would even lie at higher temperatures if the heating program would be continued with increasing temperatures. Additionally, different groups of release behaviour can be distinguished. The very similar progression of intensity curves of Ag and Te could indicate that a part of Ag could be existent in the copper samples as silver telluride. This could also explain why Ag is much better released by hydrogenation than by halogenation reactions. Co-evaporation of analytes with the matrix does not seem to play a significant role. Such a conclusion can also be drawn from Fig. 8b. Even for the elements with intensity maxima near the peak maximum of copper it can be concluded that their release is not mainly influenced by the release of the copper atoms. Such an influence would lead to a clear change of the approximately symmetric shape of intensity curves to a clearly asymmetric shape with a strong tailing

The T-program TP-ramp$_{spez}$ depicted in Fig. 8 was modified to the optimized T-program TP-part (see Table 2) which was used for all following quantitative measurements with Method M2 (partial evaporation of sub-samples). Compared with TP-ramp$_{spez}$ it has a shortened high temperature plateau which moreover starts at earlier time. At this time, after a temperature ramp (at 38 s), Se and Te are beginning to be released. A roughly impression of the release behaviour of elements using TP-part can be gained observing Fig. 9 (TP-tot) because the temperature progress is very similar up to sec. 37 where TP-part ends.

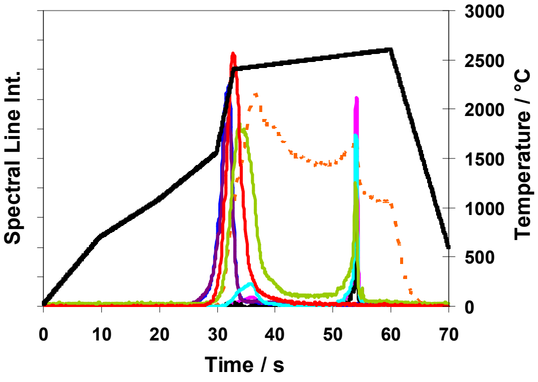


Fig. 9 Method M3 (total evaporation): Spectral line intensities with H_2 as modifier (29 % H_2; inner gas flow rate 150 mL min^{-1}) for As ▬, Au ▬, Bi ▬, Cu ▪ ▪ ▪, Pb ▬, Sb ▬, Se ▬ and Te ▬, using sub-samples of copper CRM ERM®-EB385, and temperature *T* ▬ using T-program TP-tot of Table 2.

In Fig. 9 time and temperature depending spectral line intensities of seven analytes and of copper matrix are depicted for the case of total sub-sample evaporation (Method M3) by using temperature program TP-tot (see Table 2). The very different behaviour of different groups of analytes in case of a total evaporation (Method M3) is a fact, being most noticeable in view of Fig. 9. The intensity maxima of the elements as already investigated in case of partial evaporation of sub-samples, (such as of Bi, Pb, (Se) and Te) of but also those of elements here not depicted (such as of Ag, Cd, Mg, Mn, Zn) appear in the first part of the temperature program before the copper intensity achieves its maximum, whereas the other investigated elements, which cannot be determined by Method M2, such as As, Au, Sb and Sn have their intensity maxima distinctly later. Their sharp intensity peaks appear after the last phase of copper matrix evaporation. To interpret the results of Fig. 9, it is necessary to note that the signal of copper at > 55 s is only an artefact coming from memory effects of the system. The intensities of Se and Sb have maxima at two different temperatures. Both elements have a second smaller peak in addition to the main peak; the smaller peak appears for Se in the last part and for Sb in the first part of the temperature program. The fractions of the analyte masses of the four elements released in the last phase of the temperature program (approximately expressed as fractions of their spectral line intensities) are: Sb (60 – 70 %), As, Sn (> 90 %) and Au (≈ 100 %). From first exploratory investigations it could be concluded additionally that platinum metals show release behaviour very similar to that of Au. One aspect of a succeeding publication could be further and more detailed investigations to this point.

Sample pre-treatment by "roasting"

Spectral line intensities of sub-samples of CRM BAM-385 after "roasting" at 400 °C in air for 30 min (roasted) and in original state were compared using Methods M2 and M3. No significant deviations were found in any case. It could certainly be concluded that for calibration with real copper samples, a starting roasting procedure of sub-samples is not necessary when using Methods M2 or M3 based on H_2 gas used as modifier.

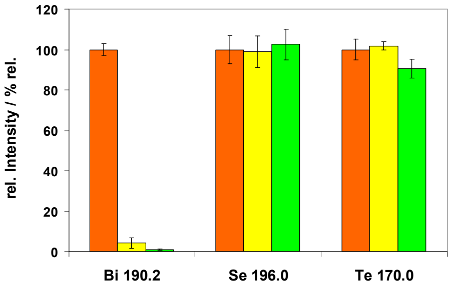


Fig. 10 Spectral line intensities of Bi, Se and Te using copper CRM ERM®-EB385 after passing the first analytical step of Method M1 (modifiers ■ SF_6 and ■ NF_3) measured in the second step of Method M1 (29% of H_2 modifier gas) standardized to the intensities without previous analytical treatment (■ no previous step of M1).

Completeness of analyte release of Se and Te

In Fig. 10 the intensities of Bi, Se and Te were measured in the second step of M1 using sub-samples which had been analyzed in the first step of M1 using SF_6 and NF_3 as halogenating modifiers (as described in the first part of this work) and compared with intensities resulting from measurements without the first step. In opposite to Bi, the analytes Se and Te can be determined very well in the second step of M1 without any losses coming from the first step; but to be on the safe side it is recommended to subject not only the analysis sub-samples but also the calibrating sub-samples to the first step of M1.

Calibration

Working conditions used are listed in Tables 1 and 2. The calibration functions were determined by using Methods M2 and M3 and five different copper CRMs, and blank measurements. Some of them are depicted in Fig. 11 as typical examples.

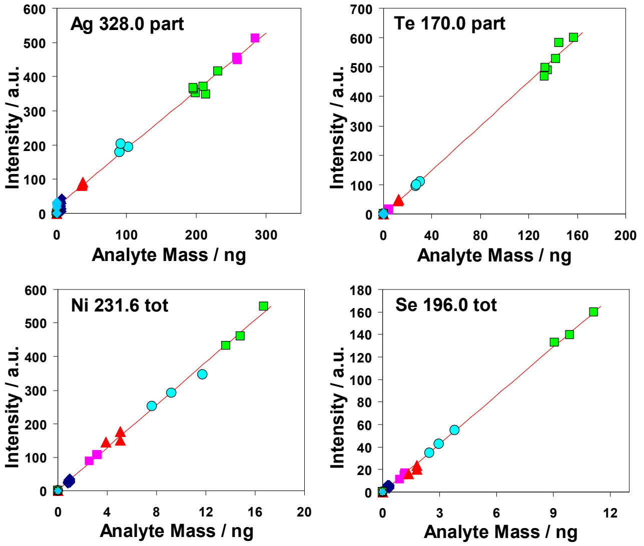


Fig. 11 Calibration functions using Methods M2 ("part") and M3 ("tot") based on varied sub-sample masses of the CRMs BAM-M381 (♦), BAM-M382 (▲), ERM®-EB383 (●), ERM®-EB384 (■) and BCR 074 (■), and on blank measurements (♦). ——— common linear regression line

The investigated calibration functions are straight regression lines; they have negligible or very low intercepts. All measured points lay very near to the common calibration functions. These facts can be interpreted as indication to a high trueness of both methods. To underpin this statement their coefficients of determination R^2 were recorded in according columns of Table 5. The majority of the values of most coefficients of determination are > 0.99.

Limits of quantification (LOQs)

The limits of quantification (LOQs) listed in Table 5 were calculated by the 9s-criterion[76] using the standard deviations obtained with real copper blank samples and with slopes of the linear calibration functions (as depicted in Fig. 11). For measurements with partial evaporation (Method M2) 10 sub-samples of about 20 mg of CRM BAM-M381 were used as blank samples. After subjecting them to the standard temperature program of Method M2 (one run) the copper globules contained no measurable analyte contents For measurements with total evaporation (Method M3) 10 sample boats were filled with a mass of about 3 mg of the CRM BAM-M381. These sub-samples could not be pre-cleaned by Method M3 in analogy to the former procedure with Method M2. These determined LOQ values are therefore assumed to be slightly higher than those which could be expected when pre-purified blank samples would have been used.

Table 5: LOQs (values > 1.0 mg kg^{-1} are marked gray) and coefficients of determination R^2 of the corresponding linear calibration functions (values < 0.99 are marked gray) determined by using Methods M2 (20 mg sub-samples, partial evaporation) and M3 (3 mg sub-samples, total evaporation). Spectrometers used: ARCOS (EOP).

Element	LOQ 9s-crit. / mg kg^{-1} and coefficients of determination (R^2)			
	part.evap.(M2)		tot. evap. (M3)	
λ / nm	LOQ calc. for 20 mg	R^2	LOQ calc. for 3 mg	R^2
Ag 243.7	1.58	0.9939	0.23	0.9867
Ag 328.0	0.03	0.9977	0.02 *)	—
As 189.0	0.17	0.9983	0.04	0.9937
Bi 190.2	0.02	0.9995	0.03	0.9992
Cd 228.8	0.03	0.9963	—	—
Fe 241.3	1.40	0.9910	1.56	0.9942
Mg 279.0	0.13	0.9902	0.97	0.9974
Mg 285.2	0.03	0.9902	0.11	0.9855
Ni 231.6	—	—	0.10	0.9985
Pb 168.2	0.03	0.9841	0.11	0.9750
Pb 283.3	0.08	0.9859	0.23	0.9427
Sb 206.8	0.22	0.9958	0.15	0.9956
Se 196.0	0.03	0.9986	0.07	0.9923
Sn 140.0	—	—	0.86	0.9982
Te 170.0	0.03	0.9989	0.06	0.9977
Zn 334.5	0.06	0.9944	0.79	0.9690

— = could not be measured (overflow of signal or signal too low); *) wave length 338.2 nm

Au is not listed because no CRM was at our disposal. An LOQ value in the low ppb level can be given as a first estimation. From the results of Table 5 high detection power for the investigated 13 analytes (15 pairs analyte/spectral line) of the investigated methods based on hydrogenation is evident. It can be concluded:The most important result is that Se and Te can be determined with very low LOQ values using all three Methods.

- Elements Ag, Mg and Ni, can also be determined with low LOQ values by Methods M2 and/or M3 using hydrogenation reactions.
- The LOQs determined for the great majority of elements/spectral lines (the three exceptions are marked gray) are lying in the sub-mg kg^{-1} region independent if Method M2 or M3 were applied.
- LOQ values below 0.1 mg kg^{-1} could be achieved for 8 elements (of 13) using Method M2
- The LOQs determined for Method M3 are for most analytes higher than those determined for Method M2 (exceptions Ag, As, Sb).

Table 6: Analytical results of copper CRMs ERM®-EB383 and BCR 074 using Methods M2 and M3. Spectrometers used: ARCOS (EOP) and ARCOS (SOP); m = mean, s = standard deviation (n=3); RSD = relative standard deviation; RD = absolute value of relative deviation of measured values from certified mass fractions. RSD and RD values > 15 rel% are marked gray.

Element, λ / nm	Cu-CRM ERM®-EB383 cert. val. *U* * / mg kg^{-1}	part. evap. (M2) SOP m / mg kg^{-1}	s	RSD / rel%	RD	tot. evap. (M3) SOP m / mg kg^{-1}	s	RSD / rel%	RD
Ag 328.0	4.70 ± 0.20	5.04	0.43	8.5	7.3	—		—	
As 189.0	1.93 ± 0.15	1.99	0.18	9.2	3.3	2.02	0.07	3.7	4.6
Bi 190.2	1.02 ± 0.09	1.11	0.03	2.3	9.3	1.06	0.02	1.6	4.4
Cd 228.8	1.48 ± 0.15	1.56	0.08	5.2	5.6	—		—	
Fe 241.3	10.9 ± 0.5	10.4	0.7	6.9	5.0	11.7	0.6	5.2	7.3
Mg 279.0	2.37 ± 0.29	2.54	0.08	3.1	7.3	2.32	0.3	12.8	2.3
Ni 231.6	3.59 ±0.21	—		—		3.48	0.20	5.6	2.9
Pb 168.2	1.31 ± 0.20	1.39	0.03	2.5	6.5	1.23	0.11	8.6	6.2
Sb 206.8	1.44 ± 0.17	1.46	0.1	7.1	1.7	1.45	0.08	5.4	0.4
Se 196.0	(1.16 ± 0.19)	1.32	0.05	3.6	13.7	1.24	0.01	0.6	7.1
Sn 140.0	4.7 ± 0.6	—		—		5.0	0.2	3.5	7.3
Te 170.0	1.40 ± 0.16	1.36	0.01	1.1	2.5	1.33	0.03	1.9	5.1
Zn 334.5	(7.8 ± 0.4)	7.5	0.1	1.5	4.3	7.7	0.6	7.7	0.8

Element, λ / nm	Cu-CRM BCR 074 cert. val. *U* ** / mg kg^{-1}	part. evap. (M2) EOP m / mg kg^{-1}	s	RSD / rel%	RD	tot. evap. (M3) EOP m / mg kg^{-1}	s	RSD / rel%	RD
Ag 328.0	12.8 ±0.7	12.8	0.3	2.1	0.2	—		—	
As 189.0	0.78 ±0.14	0.79	0.06	7.9	1.3	0.85	0.05	5.6	9.4
Bi 190.2	0.10 ±0.03	0.09	0.004	4.5	8.8	0.1	0.01	11.8	1.4
Cd 228.8	—	—		—		—		—	
Fe 241.3	1.14 ±0.06	1.03	0.21	20.8	9.7	1.23	0.56	45.7	7.7
Mg 279.0	—	—		—		—		—	
Ni 231.6	1.04 ±0.11	—		—		1.15	0.03	2.6	10.8
Pb 168.2	0.97 ±0.05	0.96	0.06	6.6	1.4	0.96	0.04	4.2	0.7
Sb 206.8	0.58 ±0.03	0.76	0.03	3.4	31.7	0.65	0.07	11.2	12.2
Se 196.0	0.37 ±0.04	0.40	0.03	8.1	7.1	0.39	0.03	7.2	4.3
Sn 140.0	<0.07	<0.1		—		<0.1		—	
Te 170.0	0.21 ±0.08	0.22	0.01	3.1	4.6	0.21	0.03	12.9	1.6
Zn 334.5	0.46 ±0.07	0.52	0.02	4.3	12.8	—		—	

- = could not be measured (overflow of signal or signal too low or analyte not certified)
( ) = indicative values in the CRM certificate
U * = expanded uncertainty with a coverage factor k = 2
U ** = uncertainty expr. as half-width of the 95% confidence interval of the certif. mean

Trueness and repeatability of results

In Table 6 values representing recovery and repeatability of the measurement of mass fractions of 13 analytes by using the different Methods (M2 and M3) are exemplarily listed. The copper CRMs ERM®-EB383 and BCR 074 were used as samples to be analyzed. The calibration was based on copper CRMs BAM-M381, BAM-M382 and ERM®-EB384 and additionally BCR 074 when ERM®-EB383 was analyzed. The mass fractions determined for the 13 investigated analytes in the CRMs by using the optimized Methods M2 and M3 show a good agreement in almost all cases with the certified mass fractions which is expressed by their relative deviations RD (relative differences of certified and measured mass fractions). These RD values - as a measure for recovery rate - were less or not much larger than 15 rel % with one exception in each method. The RSD-values have not a high statistical basis in view of the number of repeated measurements. But on the other hand the totality of all the calculated RSD values allows an assessment of repeatability of the methods used. 37 of 39 measured RSD values are lying in a region < 15 rel% - most of them are < 10 rel% and many of them are even < 5 %. This result is indicating a very acceptable level of repeatability (precision) of both methods used to determine the 13 elements. As it can be seen from Table 6 the optimized methods allow a trustable calibration for the investigated elements based on calibration with copper materials of known contents of analytes. The masses of the solid sub-samples should lie in the range of 20 mg ± 2 mg for partial evaporation and of 2 mg - 5 mg for total evaporation of the sub-samples. The developed methods are fast, requiring only two minutes for a single measurement.

Conclusions

By the results of our investigations essential answers could be given to the open questions listed in the introduction:

(1) *The necessity to apply the preliminary time consuming "roasting" (surface oxidizing) procedure*: This step can now be omitted when SF_6 or NF_3 are used as modifiers and copper CRMs are used for calibration.
(2) *The fact that not all analytes could be calibrated by using dried residua of calibration solutions*: The problem could not really be solved by using SF_6 or NF_3. CF_4 used instead of CHF_3 did not show the expected improvement. However, a high quality of analytical performance was achieved with SF_6 or NF_3 for Ag, Al, As, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Pb, Sb, Si, Sn, Ti, Zn, Zr. The analytes Ag, Mg and Ni stayed “critical”, but strongly improved results could be achieved for their determination, as described in the following item.
(3) *Some elements could not (Se, Te) or not sufficiently (Ag, Mg, Ni) be released from the matrix by halogenation reactions and could therefore not (or only limited) be determined and quantified:* This drawback was totally overcome using hydrogen as modifier. Optimized methods were developed based on partial as well as on total evaporation using hydrogenation reactions and higher temperatures than for halogenation reactions. This is true for Ag, Mg, Ni in case of partial evaporation only without any previous halogenation step (M2), or in case of total evaporation of copper samples (M3). additionally Several other elements besides Se, Te and Ag, Mg, Ni can be quantified simultaneously: Au, As, Bi, Cd, Fe, Pb, Sb, Sn and Zn, but for some of them better analytical performance can be achieved using first step of Method M1 based on halogenation reactions. Very low limits of quantification, especially for Se and Te, but also for the “critical” elements Ag, Mg, Ni, as well as high trueness and sufficiently high reproducibility of all results were achieved.

The analytical performance of the optimized methods now presented offers the possibility of a very fast comprehensive analysis of pure and high purity copper with excellent analytical performance. The physicochemical processes on which the analytical methods are based were interpreted in different passages of both parts of analytical investigations of this paper.

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References

1. J. Hassler, P. Barth, S. Richter, R. Matschat, *J. Anal. At. Spectrochem* **26** (2011) 2404-2418
2. S. P. Murarka, R. J. Gutmann, *Copper-Fundamental Mechanisms for Microelectronic Applications*, John WileySons, Inc., New York, 2000.
3. S. P. Murarka and S. W. Hymes, *Crit Rev Solid State*, 1995, **20**, 87-124.
4. P. Singer, *Semiconductor Int* 2002, **25**, 46-53.
5. E. Borowiak-Palen, A. Steplewska and M. H. Rummeli*, Phys Status Solidi B*, 2009, **246**, 2448-2452.
6. E. N. Grilli, S; Blanco FS, Sbrana, A; Zanini, A, *Das Unbekannt Edle*, Instituto Salesiano Pio XI, 2002.
7. M. Steffen, *Erzmetall*, 2002, **55**, 366-368.
8. B. Lange, S. Recknagel, M. Czerwensky, R. Matschat, M. Michaelis, B. Peplinski and U. Panne, *Mikrochim Acta*, 2008, **160**, 97-107.
9. R. Matschat, M. Czerwensky, S. Pattberg and H. J. Heinrich, *Physica Status Solidi a-Applied Research,* 2002, **189**, 107-122.
10. M. Milbourn, *J I Met*, 1934, **55**, 275-281.
11. M. Milbourn, *J I Met*, 1943, **69**, 441-463.
12. M. Milbourn, *Proc Phys Soc*, 1947, **59**, 273-275
13. G. Maassen, *Angewandte Chemie*, 1953, **65**, 113-114.
14. G. Maassen, *Angewandte Chemie*, 1953, **65**, 286-291.
15. G. Maassen, *Rev Univ Min,* 1959, **15**, 300-303.
16. R. H. Price, *Metal Ind*, 1960, **97**, 167-170.
17. W. E. Publicover. *Anal Chem*, 1965, **37**, 1680-1684.
18. P. Tymchuk, D. S. Russell and S. S. Berman, *Spectrochim Acta*, 1965, **21**, 2051.
19. P. Tymchuk, A. Mykytiuk and D. S. Russell, *Appl Spectrosc*, 1968, **22**, 268.
20. L.N. Filimonov, *Zavod Lab*, 1953, 16, 1200, **19**, 569.
21. H. Gantzkow, *Neue Hütte*, 1964, **3**, 188-190.
22. M. Mahar, G. Kunselman, P. Brown, P. Dalager and P. Perzl, *American Laboratory* January 2010
23. *European Standard*, EN 15079, 2007.
24. *European Standard*, EN 15063-1, 2006.
25. *European Standard*, EN 15063-2, 2006.
26. J. D. R. Payling, A. Bengston, *Glow Discharge Optical Emission Spectrometry*, New York, 1997.
27. T. Gusarova, V. D. Hodoroaba, R. Matschat, H. Kipphardt and U. Panne, *J Anal Atom Spectrom*, 2009, **24**, 680-684.
28. M. Kasik, C. Venzago and R. Dorka, *J Anal Atom Spectrom*, 2003, **18**, 603-611.
29. R. Matschat, J. Hinrichs and H. Kipphardt, *Anal Bioanal Chem*,, 2006, **386**, 125-141.
30. T. Gusarova, *PhD Thesis*, Humboldt University, Berlin, 2009
31. T. Gusarova, T. Hofmann, H. Kipphardt, C. Venzago, R. Matschat and U. Panne, *J Anal Atom Spectrom*, 2010, **25**, 314-321.
32. B. Lange, R. Matschat and H. Kipphardt, *Anal Bioanal Chem*, 2007, **389**, 2287-2296.

33. H. P. Weise, W. Gorner and M. Hedrich, *Fresenius' J Anal Chem*, 2001, **369**, 8-14.
34. R. Simon, G. Buth and M. Hagelstein, *Nucl Instrum Meth B*, 2003, **199**, 554-558.
35. S. Pattberg and R. Matschat, *Fresenius' J Anal Chem*, 1999, **364**, 410-416.
36. S. Pattberg, *PhD Thesis*, Humboldt University, Berlin, 1999.
37. H. Traub, M. Czerwensky, R. Matschat, H. Kipphardt and U. Panne, J *Anal Atom Spectrom*, 2010, **25**, 690-696.
38. H. Traub, M. Walle, J. Koch, U. Panne, R. Matschat, H. Kipphardt and D. Gunther, *Anal Bioanal Chem*, 2009, **395**, 1471-1480.
39. J. Wienold, H. Traub, B. Lange, T. Giray, S. Recknagel, H. Kipphardt, R. Matschat and U. Panne, *J Anal Atom Spectrom*, 2009, **24**, 1570-1574.
40. C. M. Domizel, *Modern Methods of analysis of copper and its alloys*, Amsterdam, London, New York, 1963.
41. K. Z. Balla, E. G. Harsanyi, L. Polos and E. Pungor, *Mikrochim Acta*, 1975 **I**, 107-116.
42. E. Milella, E. Sentimenti and G. Mazzetto, *Atom Spectrosc*, 1993, **14**, 1-3.
43. B. Field, *The determination of Trace Metals in High Puritiy Copper with the GTA-95 Graphite Tube Atomizer*, Varian, 1982.
44. S. A. Kumar, M. B. Sanglikar, M. S. Shaikh and M. Sudersanan, *Indian J Chem Techn*, 2004, **11**, 170-177.
45. T. D. Lopez, M. T. L. Marin and A. G. Coedo, *J Anal Atom Spectrom*, 1988, **3**, 447-452.
46. P. S. Doidge, *Determination of trace impurities in high-purity copper by sequential ICP-AES with axial viewing*, Varian, 1998.
47. S. D. Overduin and I. D. Brindle, *J Anal Atom Spectrom*, 2001, **16**, 289-292.
48. R. Matschat, M. Czerwensky, M. Hamester and S. Pattberg, *Fresenius' J Anal Chem*, 1997, **359**, 418-423.
49. R. Matschat, M. Czerwensky, S. Pattberg, H. J. Heinrich and S. Tutschku, *Mater Trans*, 2002, **43**, 90-97.
50. R. Matschat and M. Czerwensky, *Physica Status Solidi a, Applied Research*, 1997, **160**, 567-574.
51. E. J. dos Santos, A. B. Herrmann, J. L. Olkuszewski, T. D. Saint'Pierre and A. J. Curtius, *Braz Arch Biol Techn*, 2005, **48**, 681-687.
52. H. Umeda, I. Inamoto and K. Chiba, *Bunseki Kagaku*, 1990, **39**, 283-287.
53. K. Chiba, I. Inamoto and M. Saeki, J *Anal Atom Spectrom*, 1992, **7**, 115-119.
54. C. J. Park, S. R. Park, S. R. Yang, M. S. Han and K. W. Lee, *J Anal Atom Spectrom*, 1992, **7**, 641-645.
55. A. Detcheva, P. Barth and J. Hassler, *Anal Bioanal Chem*, 2009, **394**, 1485-1495.
56. S. Z. Chen, F. Li, Z. H. Liao, T. Y. Peng and Z. C. Jiang, *Fresenius' J Anal Chem,* 1999, **364**, 556-559.
57. G. Zaray and T. Kantor, *Spectrochim Acta*, *Part B*, 1995, **50**, 489-500.
58. J. Hassler, G. Zaray, K. Schwetz and K. Florian, *J Anal Atom Spectrom,* 2005, **20**, 954-956.
59. G. Zaray, F. Leis, T. Kantor, J. Hassler and G. Tolg, *Fresenius' J Anal Chem,* 1993, **346**, 1042-1046.
60. P. Barth, J. Hassler, I. Kudrik and V. Krivan*, Spectrochim Acta, Part B,* 2007, **62**, 924-932.
61. S. Z. Chen, *Spectrosc Spect Anal*, 2005, **25**, 1697-1699.
62. H. Nickel, Z. Zadgorska and G. Wolff, *Spectrochim Acta*, Part B, 1993, **48**, 25-38.
63. J. A. C. Broekaert, M. A. Amberger, *J Anal Atom Spectrom*, 2010, **25**, 1308-1315.
64. K. C. Friese and V. Krivan, *Fresenius' J Anal Chem*,, 1999, **364**, 72-78.
65. O. Werner, *Fresenius' J Anal Chem*, 1963, **198**, 70-79.
66. H. Tolle, *Fresenius' J Anal Chem*, 1968, **240**, 162-170.
67. J. M. Ren and E. D. *Salin, Spectrochim Acta, Part B* , 1994, **49**, 555-566.
68. M. E. Rybak and E. D. Salin, *Spectrochim Acta, Part B*, 2001, **56**, 289-307.
69. K. C. Friese, U. Watjen and K. H. Grobecker, *Fresenius' J Anal Chem*, 2001, **370**, 843-849.
70. T. Kantor, *Spectrochim Acta, Part B,* 1988, **43**, 1299-1320.
71. P. Barth, S. Hauptkorn and V. Krivan, *J Anal Atom Spectrom*, 1997, **12**, 1359-1365.
72. IRMM European Commission, JRC, *Certified Reference Material,* Certificate BCR$^{®}$– 074 https://ec.europa.eu/jrc/sites/default/files/rm/BCR-074_cert.pdf
73. BAM Federal institute for Materials Research and Testing, Germany, *Copper CRM certificates* (http://www.rm-certificates.bam.de/de/certificates/non_ferrous_and_alloys/copper/index.htm)
74. J. Mandel, J Qual Technol, 1984, 16, 1-14.
75. DIN Standard 38 402 71, 2002
76. DIN Standard 32645, 2008
77. W. Reichel , B. G. Bleakley, *Anal. Chem.*, 1974, **46**, 59–61
78. G. Schulze, R. Martens-Menzel, *J Anal Chem,* 1993, **346**, 663-666
79. J. D. Mullen, *Talanta*, 1976, 23, 846-848
80. P. Grünwald, P. Tschöpel and G. Tölg, *Z. Anal. Chem*, 1976, **279**, 187-193
81. J. Dedina, L. Dimiter, *Hydride Generation Atomic Absorption Spectrometry*, J. Wiley and Sons Ltd., U K (1995) (2015)
82. Hui Ming Liu, Shi-Yang Chen, Pin-Hsuan Chang and, Suh-Jen Jane Tsai, *Analytica Chimica Acta* . 2002. **459**, 1161–168
83. R. Bye, *Anal. Chem.*, 1985, **57**, 1481–1482
84. I. Rojas, M. Murillo, N. Carrión, J. Chirinos, *J Anal Bioanal Chem,* 2003, **376**, 110-117
85. M. Grotti, C. Lagomarsino and R. Frache, *J. Anal. At. Spectrom.*, 2005, **20**, 1365-1373
86. G. Tyler, A. Cosnier, S. Velasquez, A. Bartha, M. Ballók, *Horiba, Technical Reports, JY Division*, Feature Article Engl. **Ed. 7**, 38-43
87. H. Yamaguchi, S. Itoh, Sh. Igarashi, K. Naitoh, R. Hasegawa, *Fresenius' J Anal Chem*, 1998, **362,** 395-398
88. N. Sadiq, D. Beauchemin, *Analytica Chimica Acta,* **851,** 2014, 23-29
89. W. Nischkauer, E. Herincs, M. Puschenreiter,W. Wenzel, A. Limbeck, *Spectrochim Acta, Part B*, 2013, **89**, 60-65
90. F. Kaveh and D. Beauchemin, *J. Anal. At. Spectrom.*, 2014, **29**, 1371-1377
91. T. Vogt, D. Bauer, M. Neurot, M. Otto, *Fuel,* **152,** 2015, 96–102