


# Multiple-Choice Questions for Teaching Quantitative Instrumental Element Analysis: A Follow-Up

## Journal Article

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# Multiple-Choice Questions for Teaching Quantitative Instrumental Element Analysis: A Follow-Up

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## PART A

### Content

1. Single-choice questions
  - General Analytical Chemistry, Sampling and Sample Preparation
  - Atomic Absorption and Emission Spectroscopy
  - Inductively Coupled Plasma Mass Spectrometry
2. Multiple true-false questions (kprime type)
  - General Analytical Chemistry, Sampling and Sample Preparation
  - Atom Absorption and Emission Spectroscopy, Inductively Coupled Plasma Mass Spectrometry, and X-Ray Fluorescence Spectroscopy
  - Scope of Element Analysis
  - X-ray Fluorescence Analysis

### Notes

- This list has been compiled with great care. However, neither the author nor the publisher assumes any liability for the accuracy of the information, typos, printing errors, etc.
- The questions listed here were developed in for a specific course in quantitative instrumental element analysis (see Supplementary Information Part B) and translated from original German into English.
- The position of the accepted option (key) can often be varied to achieve “key balancing”, i.e. keys at random positions, with the exception of options in logical order (e.g. from low to high values).
- The option “I don't now” may be used for all questions in formative contexts (see Schwarz, G. Questions For Classroom Response Systems and Teaching Instrumental Element Analysis. *Chimia*, **2021**, *75*, 33-38, DOI: 10.2533/chimia.2021.33).
- If not otherwise noted, all questions are intended to be used in a „best-option-mode“. That is to say, that (a) students should select not just a correct option, but the best and (b) if students identify a “correct” option, they still should look out for a better option.
- Additional notes to specific questions can be found at the end of the document.

### Abbreviations

AAS	Atomic absorption spectroscopy
cps	counts per second
EDX	Energy dispersive X-ray fluorescence
ETV-AAS	Electrothermal vaporization atomic absorption spectroscopy
ICP	Inductively coupled plasma
ICP-MS	Inductively coupled plasma optical mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectroscopy
<i>m/z</i>	mass-to-charge ratio
WDX	Wavelength dispersive X-ray fluorescence
XRF	X-ray fluorescence spectroscopy

# 1. Single-choice questions

## General Analytical Chemistry, Sampling and Sample Preparation

- 1. A mass fraction of 1 µg/g (1 ppm) iron corresponds to ca.  $1.08 \cdot 10^{16}$  iron atoms (or ions) per gram of sample. A mass fraction of 1 µg/g lithium in the same sample means...**
- A less atoms.  
B an equal number of atoms.  
C more atoms.
- 2. You want to analyze a delivery of bulk cargo. Which procedure is more adequate?**
- A Take 20 samples, mix them and measure once.  
B Take one sample and measure 20 times.  
C It makes no difference.
- 3. You receive a powdered chocolate sample to determine cadmium. Approach 1: You take 100 mg of powder FIVE times, digest and dilute the portions separately and measure each ONCE. Approach 2: You take 100 mg of powder, digest and dilute the portion and measure the resulting solution FIVE times. Which approach leads to an improved precision of the result?**
- A Approach 1  
B Approach 2  
C It makes no difference.
- 4. What are the main products formed during the digestion of chocolate with nitric acid and hydrogen peroxide?**
- A Air and water  
B Carbon dioxide and water  
C Nitrogen and water  
D Nitrogen and carbon dioxide  
E Carbon, nitrogen, and hydrogen
- 5. A chocolate sample was digested in a closed vial under pressure using nitric acid and hydrogen peroxide using a microwave system. The resulting solution was filled up with diluted acid. What constitutes the main matrix of the analyte cadmium in the prepared solution after the digestion of chocolate?<sup>2,3</sup>**
- A Cacao, sugar, fat  
B Water  
C Cadmium ions  
D No matrix
- Key Explanation**
- C *The difference in number of atoms results from different atom masses. Lithium has about an eighth of the atomic mass of iron. Hence, within the same sample, if the same mass fraction of iron and lithium is present, it results in more lithium atoms present.*
- A *The risk of an unrepresentative sample is high with option B. This would lead to a systematic bias. Although this may not be impossible with option A (e.g. if the samples are not taken randomly from the entire volume), but the risk is much lower than with option B. If in doubt, take more samples and measure them less than vice versa. Of course, all depends on the specific analytical problem.<sup>1</sup>*
- A *Approach 2 provides the lower precision (i.e. the standard deviation is higher) in the result, because the same solution is measured and only the random error of the measurements affects the precision. With approach 1 also the random error of the sampling and sample preparation lead to deviations. Note: Although approach 2 leads to better result precision, for the overall quality of the analytical result, approach 1 needs to be followed (compare with question 2). There should be no difference for homogeneous samples.*
- B *Chocolate mainly contains sugar, fat, and proteins, meaning organic compounds which mainly contain carbon, hydrogen, oxygen and some nitrogen. Nitric acid and hydrogen peroxide act as oxidizing agents. Therefore, carbon dioxide and water are formed during the digest. The nitrogen in the sample forms nitrate.*
- B *The term matrix refers to the components of a sample other than the analyte. It can vary drastically between the sample (i.e. chocolate) and the sample prepared for measurements. After sample digestion, the compounds are no longer present. Option A would be the correct option in case of the original sample (compare with question 4).*

6. a) After the determination of cadmium in a bar of chocolate, can a statement be made on the basis of the result as to whether it is healthy to consume this chocolate?

- A No, because only cadmium was determined.
- B Yes, as long as the legal limit for cadmium content is not exceeded.

A *Cadmium is only one potential risk. Hence, just based on the determination of the cadmium is not sufficient to assess the safety of consuming this chocolate.*

b) Can conclusions be drawn about the cadmium content of the chocolates of this type/trademark based on the analysis shown or its results?

- A Yes, if it was analyzed correctly.
- B No, more samples are required.

B *As they say "One measurement is no measurement." A single sample is just not sufficient to make any statement as this sample could be an outlier in terms of the general cadmium content of this type of chocolate or trademark.*

c) Now, you would like to determine cadmium content in a chocolate with nuts. Do you remove the nuts from the chocolate before analysis?

- A No, the nuts are also consumed.
- B Yes, cadmium is in chocolate, not nuts.
- C No, additional cadmium is located only on the nut's surface.

A *The nuts are also part of the chocolate, they are consumed as well and potentially also contain cadmium. The general aim is to determine whether the product's consumption is safe with regards to the cadmium content as part of a typical diet. It is interesting to note, that regulations forbid manufacturers to "dilute" food products in order to comply with limits. For example, they are not allowed to put cadmium-free nuts into chocolate, which in itself contains too much cadmium.*

7. For the risk assessment of soil samples due to heavy metals, the samples are "rolled" in water or dilute acid (i.e. the slurry is continuously moved over several hours).

a) What is the purpose of "rolling" the sample?

- A Extraction of dissolvable heavy metals.
- B Homogenizing the sample.
- C Separation of different particle densities and sizes.

A *The aim is not to determine the total content of heavy metals, but the amount which can be released, e.g. due to acid rain, and are then bioavailable. This is an approximation. Hence, this procedure intends to extract heavy metals from the soil sample.*

b) Which part is used for analysis after "rolling"?

- A Solids
- B Solution

B *Subsequently, the extracted analytes, i.e. heavy metals, are present in the solution, which is therefore used for further analysis.*

c) Will a digestion of this part be carried out afterwards?

- A Yes
- B No

B *Since the analytes are already in solution at this point, no further digestion is performed.*

8. You perform a total digestion of a reference material using a mixture of HNO<sub>3</sub> and HCl in a beaker on a hot plate. But you determine less tin than certified. Why?

- A Chloride decomposes tin.
- B Tin chloride is volatile.
- C The acid mixture oxidizes tin.
- D The acid mixture reduces tin.

B *Tin chloride (e.g. formed with the chloride from HCl) is volatile and may be lost during an open hot plate digestion. The acid mixture is neither able to decompose (nuclear reaction!?) or reduce tin. Even if tin is oxidized, this would not necessarily lead to a loss of analyte, since tin would remain in solution.*

9. How do you prepare a sample of salmon to differentiate between and quantify organic mercury species?

- A Microwave digestion using HCl and H<sub>2</sub>O<sub>2</sub>
- B Microwave digestion using HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>
- C Microwave digestion using HNO<sub>3</sub>
- D No digestion

D *If different organic compounds need to be determined separately, an acid digestion would decompose those and make such an analysis, i.e. speciation, impossible. Extracting these compounds would be adequate.<sup>4</sup>*

10. Standard addition is used to circumvent or minimize interferences. Which interferences **CANNOT** be corrected by standard addition?

- A Matrix effects
- B Spectral interferences
- C Non-spectral interferences

B Spectral interferences are not factored in when using standard additions for calibration because they are additive and not multiplicative.

11. What is a requirement for an internal standard?<sup>5</sup>

- A Both standards and samples need to contain the internal standard in the same concentration.
- B The analyte reacts quantitatively with the internal standard.
- C The measurement needs to be able to distinguish between the analyte and internal standard.

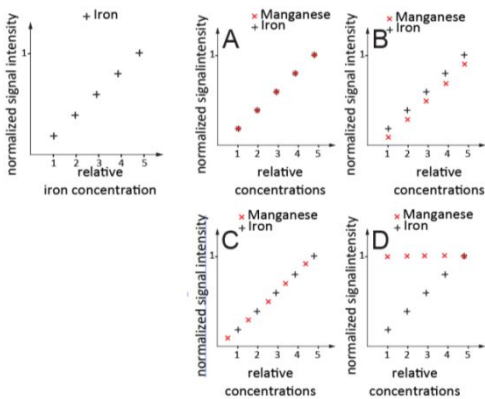
C Both the analyte and the internal standard need to be detected separately, i.e. result in independent signals. Although it is routine practice to have the same concentration of internal standard in standards and sample, this is not a requirement. It often is sufficient to either know the different internal standards concentrations or their ratios. It is crucial that analyte and internal standard do not react with each other; the same goes for components introduced with the internal standard, e.g. counterions, which may precipitate with the analyte.

12. Which of the following affects selectivity?

- A Contamination
- B Disturbance of sample introduction
- C Excitation interferences in the plasma
- D Spectral interferences

D Selectivity is the ability of a method to determine particular analytes in mixtures or matrices without interferences from other components of similar behavior. Among these options only spectral interferences affect the selectivity. The other may influence the signal and thereby the result of the analysis, but not the capability of the measurement/method to distinguish between an analyte and other matrix components, i.e. selectivity.

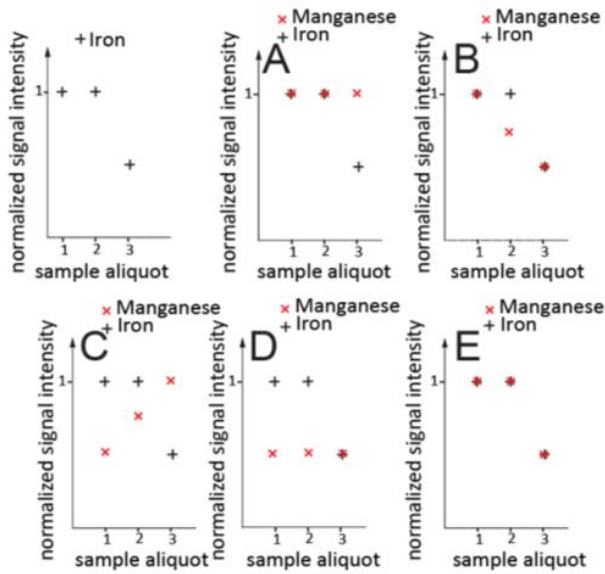
13. a) Basics for the use of internal standards: For determining iron, manganese is added to all calibration solutions so that manganese is present at the same mass fraction. The signal intensities for iron are depicted (top left). Which signal intensities do you expect for manganese?



- A
- B
- C
- D

D Since manganese has the same mass fraction in all solutions, the signal intensity is expected to be the same for all solutions. A deviation will only occur if other circumstances interfere (clogging of the nebulizer, different matrix effects with different samples, etc.).

b) Subsequently, three aliquots with the same iron concentration are measured. During the measurement of the third aliquot the nebulizer gets clogged and the iron signal only has half of its intensity (top left). Which signal intensities do you expect for manganese?



- A
- B
- C
- D
- E

E Absent other effects, the clogging of the nebulizer affects iron and manganese signals in the same manner.

c) Following-up on the two previous questions: You have a sample and a reference solution, but there is less manganese as an internal in the sample solution (opposite to the standard solutions) than designated. What will be a consequence?

- A This leads to a larger random error.
- B This leads to a larger systematic error.

B Because the quantification of iron uses the signal ratio of iron and manganese, the result will be affected by the lower amount of manganese in a systematic manner. If – as assumed in the question – the amount of manganese is lower than designated, the quantified amount of iron will be too high.

14. a) You determine lead in children's toys after acid digestion of samples and dilution of the resulting solutions with ICP-OES with external standards. You determine a limit of detection of 15 µg/kg lead for these solutions. How does this relate to the limit of detection in children's toys? The limit of detection in children's toys is...<sup>6</sup>

- A lower.
- B equal.
- C higher.

C Due to sample preparation (i.e. dilution) the limit of detection of lead in the children's toys is higher.

b) You ask yourself whether the measurement is affected by a matrix effect. Which experiment helps to investigate this question? Check all correct options.

- A Spike the sample with a known amount of lead.
- B Spike the sample with bismuth.
- C Compare sensitivities of external calibration and standard addition.
- D Measure a certified reference material with a known lead concentration.

A, C Matrix effects alter the sensitivity (slope of calibration function). These differences can be investigated with option C. Option A can also reveal differences if signals prior and post addition of lead are compared, which is essentially the same approach as standard addition. Options B and D do not investigate a difference in sensitivities specifically and are therefore not suitable.

c) To reduce the amount of acid after digestion for measurement, you evaporate the solution and dissolve the residue in diluted acid. How do you check if this leads to loss of lead? Check all correct options.

- A Spike the sample with a known amount of lead.
- B Spike a blank sample with lead.
- C Spike a blank sample with bismuth.
- D Measure a certified reference material with a known lead concentration.

B, D *For Option A to work, the amount of lead in the samples must be known, which is not the case. Option C cannot assume that bismuth and lead behave the same, which is unlikely given the properties of the lead compounds that can form during acid digestion. Note that the reference material should be matrix-matched with the sample, otherwise the matrix may have an effect on lead loss.*

15. You do not have a reference material for lead in wood. What would be the closest match?

- A Lead in cellulose
- B Sugar of lead (lead acetate)
- C Lead in hair
- D Pure lead

A *Only lead in cellulose is matrix-matched. Lead in hair provides an organic matrix, but the match is not as good. The lead content of lead acetate is much higher than in wood. This would need to be diluted, preferably with an organic matrix.*

16. You participate in a round robin test to determine mercury in powdered milk and find much less mercury in the samples than all other laboratories. Which approach is **NOT** suitable to investigate whether you (a) determined the correct amount of mercury and (b) the sample was an outlier?

- A Exchange samples between the laboratories
- B Analyze new samples sent by the leading laboratory
- C You reanalyze samples with a different method.

C *C is the least suitable since the sample itself may be an outlier and not the method/measurement. A and B do take this into account. Note: This is based on a true story. One laboratory determined much lower mercury concentrations in mild powder than all others (all other results were consistent). The single lab insisted on the accuracy of its results. Samples were exchanged and new samples provided. It turned out that all other samples had been contaminated by laboratory air (mercury residues; mercury diffuses rather readily through packaging like foil).<sup>7</sup>*

## Atomic Absorption and Emission Spectroscopy

17. Absorption lines of atoms<sup>8</sup> are much narrower than those for molecules. Why?

- A There are more electrons in molecules, which can be excited.
- B Molecules have vibrational and rotational modes.
- C There are more atoms in molecules.

B *The overlapping of electronic states with vibrations and rotations in molecules lead to much broader absorption lines (i.e. bands) in molecules compared to atoms.*

18.a) Where does the energy, which is absorbed by sodium when analyzing sodium with flame AAS, originate from?

- A Free atoms
- B Hollow cathode lamp
- C Thermal excitation in the flame

B *In AAS, the free gaseous atoms in their ground state absorb the radiation originating from a light source, e.g. typically a hollow cathode lamp.*

b) Where is this energy stored in the atoms?

- A HOMO(→LUMO)
- B Electrons
- C Atom nucleus

B *The valence electrons absorb the energy, leading to an electronically excited state of the atom. Since they are not part of a molecule, gaseous free atoms have no highest or lowest occupied molecular orbital (HOMO, LUMO).*

c) How is the absorbed energy released afterwards?

- A Return to the initial state through emission
- B Return to the initial state through collisions with other atoms
- C Bond excitation

A *The most common path of relaxation for electronically excited free atoms is emission. Since they are not part of a molecule, gaseous free atoms cannot excite bonds.*

**19. You try to determine chromium in a powder directly using ETV-AAS (i.e. without acid digest) but the absorbance is too high because the sample contains too much chromium. What can you do? (Select all correct options.)**

- A Use less sample per measurement
- B Add matrix modifier
- C Use a different wavelength
- D Use background correction

- A Typically, the signal is too weak, close to the detection or quantification limit and you need to increase sensitivity. But, the opposite case (too intense signal) may also occur.
- and
- C

*A: Less sample leads to less chromium atoms within the beam path during measurements and thereby lower signal.*

*B: The addition of a matrix modifier does not directly influence the amount of chromium atoms in the beam path during measurements. With typical matrix modifiers the amount increases.*

*C: The signal (absorbance) depends on the measurement wavelength. A less sensitive wavelength may provide a suitable measurement range for this measurement.*

*D: The background correction may influence the (net) signal, but this does change the fact that the chromium signal is too intense.*

**20. In flame AAS, the analyte emits light during relaxation at the same wavelength as the absorption occurs. Why does this not affect the measurement?**

- A The emission intensity of the lamp is higher than the flame's.
- B There is a time delay between absorption and emission.
- C Only the absorption is measured, not the emission.
- D The emission occurs in all directions.

- D *Emission occurs in all directions, of which the spectrometer only observes a small portion along the beam path and therefore the emission is negligible if the concentration is not too high. The time delay is much too short to have an effect. The detector can only detect the number of photons and not distinguish between sources, hence not distinguish between "not absorbed" and "emitted" photons.*

*Note, there are other reasons: E.g., the emission is less abundant than the absorption due to multiple relaxation pathways and the calibration also takes this effect into account.*

**21. If a given sample leads to formation of additional particles within the flame of an AAS instrument. Does this affect the results?**

- A Yes, the resulting analyte concentrations are too high.
- B Yes, the resulting analyte concentrations are too low.
- C No, there is no change.

- A *The hollow cathode lamp radiation is scattered unspecifically at those particles. This leads to an increase of extinction and thereby to an increase of apparent analyte concentration.*

**22. With a flame test: How do you know whether a sample contains sodium?**

- A Wavelength
- B Signal intensity
- C Signal width

- A *The wavelength(s) of the emission contains qualitative information, i.e. which element(s) a sample includes, because those emit on different wavelengths after being thermally excited (by flame or plasma). The higher the content the more intense is the radiation at those wavelengths. The signal width does not contain direct analytical information with respect to the analyte.*

**23. Can you differentiate uranium and thorium with atomic emission spectroscopy?<sup>9</sup>**

- A Yes, because they emit on different wavelengths.
- B Yes, because they have different ionization energies.
- C Yes, because they have different nuclear charges.
- D No, because they have the same energy levels.
- E No, because they emit on different wavelengths.

- A *Despite their close proximity in the periodic table, the structures of the electron shells of uranium and thorium are more than sufficiently different that after excitation by the plasma the atoms or ions returning to electronic ground states emit at different wavelengths, which can be used to determine them independently from each other.*



**24. What percentage of argon atoms is ionized in an [analytical] inductively coupled plasma?**

- A A very small percentage
- B About half
- C Almost 100%
- D 100%

A *Even at high temperatures, only a very small amount of argon is ionized. This can be approximated using the Saha equation.*

**25. Stable plasmas can also be sustained with helium instead of argon. Why is argon preferred for an ICP?**

- A Price
- B Ionization energy
- C Excitation potential
- D Argon is chemically inert

A *Helium is more expensive than argon (by about a factor 5 as of writing this manuscript) and a material in high demand and with limited sources. The high gas flows used for an ICP make helium plasmas uneconomical for routine analysis. Still, helium plasmas can be beneficial in certain applications. For example, fluorine has an excitation potential too high for argon, but within the range for a helium plasma. In analytical chemistry smaller microwave induced helium plasmas are in use, e.g. as detectors for gas chromatography.*

**26. Which principle is the basis for analyses by ICP-OES?<sup>10</sup>**

- A Absorption of light by atoms with detection of fluorescence upon transition to the ground state.
- B Thermal excitation of atoms in the gas phase with detection of emission photons upon transition into the ground state.
- C Excitation of atoms in the gas phase by the induction coil with detection of emission rays upon transition into the ground state.
- D Knocking electrons out of argon in a high-frequency plasma and absorption of these electrons by analyte atoms with detection of emission rays upon transition into the ground state.

B *B is the best option, which represents the principle of ICP-OES well enough; all others have flaws: ICP-OES is not based on absorption of radiation/light/electrons; although an alternating field from the induction coil is used to sustain the plasma, this is irrelevant for the principle of ICP-OES.*

**27. ICP-OES: The sample introduction into the ICP is carried out as fine droplets. Assuming it is possible to introduce the same sample flow as much larger droplets into the plasma without extinguishing the plasma: Would the analyte signal change?<sup>10</sup>**

- A Yes, higher intensity.
- B Yes, lower intensity.
- C No change.

B *The plasma energy and the droplets' short dwell time within the plasma are not sufficient to vaporize, atomize and eventually excite the analytes in the same manner when larger droplets are introduced. Hence, a lower signal intensity is detected.*

**28. ICP-OES: You aim to determine 20 heavy metals in the wastewater of a production plant on a regular basis. Which spectrometer type would you use?**

- A Simultaneous
- B Sequential

A *For routine analyses, i.e. analyses with similar or equal requirements in terms of analytes and sample matrices, a simultaneous spectrometer (e.g. with fixed detectors for selected wavelengths) is preferred for many analytes due to shorter measurement times. However, if neither the sample amount consumed during analysis or overall measurement time is not of great concern, a simultaneous spectrometer will do just fine.*

**29. How often does the sensitivity of an ICP-OES instrument need to be calibrated?**

- A Yearly
- B Weekly
- C Daily
- D For each measurement session

D *A calibration needs to be performed for every analysis, i.e. every change of matrix or analyte. During longer measurement sequences, additional quality checks, e.g. with one calibration standard solution, are required.*

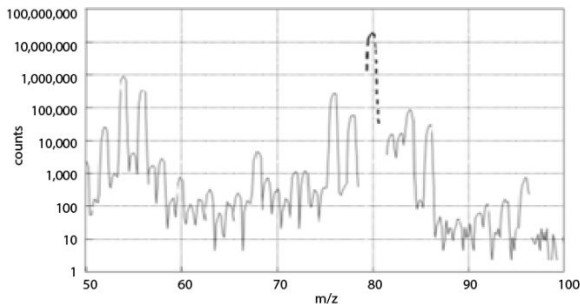
30. Compared to radial observation the emission intensity in ICP-OES is higher when using axial observation because...

- A the optical beam path is hotter.
- B of more atoms and ions in the observation zone.
- C argon diffuses into the optical beam path.

B *Radial observation comprises only a slice of the plasma. In contrast, axial observation includes a much larger volume. Therefore, there are more atoms and ions to be observed.*

## Inductively Coupled Plasma Mass Spectrometry

31. ICP-MS: What causes the signal at  $m/z$  54?<sup>11</sup>



*ICP mass spectrum of an arctic ice water sample.*

- A  $\text{ArN}^+$
- B  $\text{O}_3^+$
- C  $(\text{H}_2\text{O})_3^+$
- D  $\text{Cr}^+$
- E  $\text{Fe}^+$

A  *$\text{ArN}^+$  is a typical spectral interference. In an ICP, several argon species are formed with sample components or ambient air, leading to spectral interferences. Oxygen or water clusters are unlikely due to instability. Furthermore, the signal pattern does not match the isotopic pattern of iron or chromium.*

32. In solution iron may occur in different oxidation states. Is it possible to directly determine the ratio of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in water by ICP-MS?<sup>11</sup>

- A Yes
- B No

B *Independent of the oxidation state of iron in the sample solution, the plasma conditions alter its oxidation state (and other elements), so that usually singly charged ions dominate in ICP mass spectra.*

33. ICP-MS: Collision/reaction cells reduce...

- A systematic errors.
- B random errors.

A *While collisional damping can reduce noise as well, collision/reaction cells are mainly utilized to reduce spectral interferences and thereby systematic errors.*

34. Silver has a mass of 107.87 g/mol. At which  $m/z$  do you detect silver with ICP-MS?<sup>12</sup>

- A 106
- B 107
- C 108
- D 109

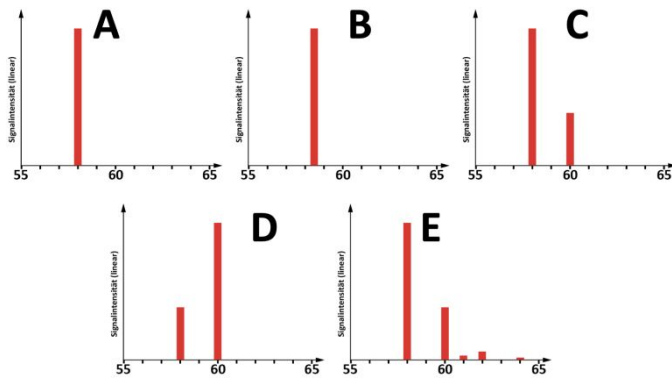
B and D *Silver has two stable isotopes,  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ , in about equal proportion, which gives an average of ca. 107.87 g/mol. Elements are detected in ICP-MS based on isotopes, they need to be detected on the corresponding  $m/z$  values.*

35. ICP-MS: What can be detected at  $m/z$  220?<sup>13</sup>

- A  $^{220}\text{Bg}^+$
- B  $^{202}\text{Hg}^{16}\text{O}^+$
- C  $^{206}\text{Pb}^{16}\text{O}^+$
- D Background
- E Nothing

D *There is no element with the symbol Bg. In the isotope table Bg denotes background. Since  $m/z$  220 is generally free of interferences (one exception is  $^{204}\text{Pb}^{16}\text{O}^+$ ), this value is useful to determine general background signal (e.g. detector noise).*

36. What signal pattern do you expect when measuring nickel with ICP-MS?



- A
- B
- C
- D
- E

E ...according to the isotope abundance distribution of nickel.

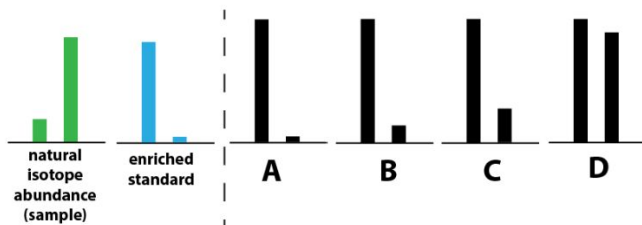
37. You measure 100,000 cps on  $m/z$  56 for an aqueous 1 ppb iron solution using ICP-MS. What signal do you expect if iron is present in the solution as a ferrocene complex?\*

\* Spectral interference are excluded.

- A A much larger signal
- B Same signal
- C A much smaller signal

B The plasma is energetic enough to atomize and ionize all element species equally. Thus, the determination of elements in such complexes can be properly calibrated using simple aqueous standards. Only in high concentrations do matrix effects occur.

38. Which isotope distribution do you expect for a 1:1 mixture of sample and standard?



- A
- B
- C
- D

D The isotope distribution in the mixture results from adding the isotope abundances of the components.

39. The isotope distribution of Europium is a 1:1 ratio ( $^{151}\text{Eu}$ : 47.8% and  $^{153}\text{Eu}$ : 52.2%). For determining Europium in a sample, you add a pure  $^{153}\text{Eu}$  standard containing 1  $\mu\text{g}/\text{kg}$  in a mixing ratio of 1:1 and obtain the following intensities:

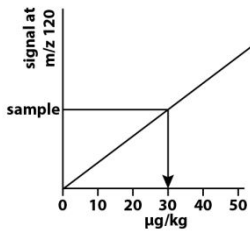
$m/z$  151: 100'000 cps  
 $m/z$  153: 150'000 cps

What is the approximate mass fraction of Europium in the sample?

- A 0.5  $\mu\text{g}/\text{kg}$
- B 1.0  $\mu\text{g}/\text{kg}$
- C 1.5  $\mu\text{g}/\text{kg}$
- D 2.0  $\mu\text{g}/\text{kg}$
- E 4.0  $\mu\text{g}/\text{kg}$
- D 10  $\mu\text{g}/\text{kg}$

E Note that (a) Eu consists of two isotopes and therefore signals for both need to be taken into account for the total mass fraction of the sample and (b) only  $^{153}\text{Eu}$  was added. The original isotope ratio is about 1:1, i.e. 100,000 cps for both  $m/z$  151 and 153. If 1  $\mu\text{g}/\text{kg}$   $^{153}\text{Eu}$  results in an additional 50,000 cps on  $m/z$  153, the original sum of  $m/z$  151 and 153 of 200,000 cps corresponds to about 4  $\mu\text{g}/\text{kg}$  Eu in the sample.

40. You quantify tin in a sample with ICP-MS and external calibration at  $m/z$  120. The isotope abundance of  $^{120}\text{Sn}$  is about 33%. The calibration for the signal at  $m/z$  120 indicates a mass fraction of  $30\ \mu\text{g}/\text{kg}$  (see figure). What is the mass fraction of tin in the sample [i.e. measurement aliquot]?<sup>14</sup>



- A  $90\ \mu\text{g}/\text{kg}$
- B  $60\ \mu\text{g}/\text{kg}$
- C  $30\ \mu\text{g}/\text{kg}$
- D  $10\ \mu\text{g}/\text{kg}$

C *It is crucial that the same isotopic distribution of tin is present in both sample and standard. Then, the  $^{120}\text{Sn}$  amount in the standard also causes a signal on  $m/z$  120 that corresponds exactly to the amount in the sample and a correction of the isotope content is not necessary. Compare with question 39.*

## 2. Multiple true-false questions (kprime type)

The questions below are kprime-type multiple choice questions. See Krebs<sup>15</sup> for details. Students need to assess each statement individually. All statements may be false or true. For formative assessment, each of the options may be put to students separately, i.e. not in a set of four. Some of the items below may be intermixed between questions as far as the context and stem allow. In cases where no specific question or instruction is provided, "Access the following statements." may be added to the stem. Further below, there are two lists of statements, addressing the scope of methods introduced in the course and XRF (see Supporting Information Part B), which use the same stem.

### General Analytical Chemistry, Sampling and Sample Preparation

#### 1. General analytical chemistry. Assess the following statements.

A The specific approach for an analysis depends on the question at hand.

Key  
true

#### Explanation

*As basic principle in analytical chemistry; that is to say that there is not a universal approach to a chemical analysis and this is depending on the (analytical) question to be addressed. Even with the same analyte and object of interest, the approach may differ for different questions. E.g. the sampling depth to determine the requirement for soil fertilization depends on the depth of the roots of a cultivar.*

B The sensitivity of a method is the signal intensity per analyte amount.

true

*by definition*

C Quantifications by ICP-OES are based on the Lambert-Beer law.

false

*With ICP-OES the emission is detected. The Lambert-Beer law describes the extinction of signal due to absorption.*

D The dilution of a sample lowers the limit of detection of the instrument.

false

*In contrast to the limit of detection of the entire method, the instrumental limit of detection is generally independent of the sample dilution factor. Note, that the instrument's limit of detection can be lower if the the undiluted solution causes signal suppression.*

#### 2. Which of the following steps can influence the accuracy of an analysis?

A Sampling

true

*Examples: unrepresentative or unsuitable sampling*

B Sample preparation

true

*Examples: sample contamination or loss of analyte*

C Measurement

true

*Examples: insufficiently matrix-matched standards, spectral interferences*

D Data analysis

true

*Examples: inappropriate calibration function, mixed up data points*

#### 3. Which sampling method can be suitable to determine the alloy type and composition of an antique knife?

A Drill out a small fraction of the metal [a few mg]

true

*Even with valuable objects, the withdrawal of a small sample may be justified (cost-benefit analysis). Representative sampling might be ensured by sampling different spots.*

B Laser ablation

true

*With laser ablation the removed amount can be further reduced and directly coupled to a detection technique, e.g. laser induced breakdown spectroscopy (LIBS) or inductively coupled plasma mass spectrometry (ICP-MS).*

C Complete digest

false

*A complete digestion destroys the (valuable) object unnecessarily.*

D Wipe with a moist cloth

false

*Even if small sample amounts can be taken, this only samples the surface and a representative sampling is questionable at best.*

**4. While determining a platinum complex in blood samples you add a known amount of palladium to all samples during sample preparation. Palladium can now be used...**

- |   |  |       |   |
|---|--|-------|---|
| A | ...for quantification of platinum according to the standard addition method. | false | <i>For calibration according to the standard addition method, the analyte platinum needs to be added, not palladium.</i>  |
| B | ...to determine the recovery rate after sample digestion.                    | true  | <i>A recovery rate can be determined by comparison of the added palladium prior to digestion and the quantified amount of palladium after sample digestion.</i> |
| C | ...to ascertain the sample uptake during the measurements.                   | true  | <i>With known amounts of spiked Pd, the sample uptake during the measurement can be observed and problems such as nebulizer clogging detected.</i>              |
| D | ...as an internal standard.  | true  | <i>Palladium need to be distinguished from the analyte during the measurement and can then be used as internal standard.</i>                                    |

**5. Analysis of titanium in wall paints compared with reference values shows values that are too low. Which actions are suitable to identify potential causes?**

- |   |  |       |   |
|---|--|-------|---|
| A | Reanalyze prepared samples again to increase precision | false | <i>Reanalyzing prepared samples with increased precision will not alter the mean.</i>                                       |
| B | Determine the recovery rate of the sample digestion    | true  | <i>A low recovery rate based on analyte loss would explain too low values.</i>  |
| C | Decrease the calibration range                         | false | <i>This does not investigate potential causes.</i>  |
| D | Add titanium to the samples to balance the difference  | false | <i>This would not alter the titanium amount in the object of investigation and thereby the analyses would remain false.</i> |

**6. Sampling and sample preparation**

- |   |   |       |  |
|---|---|-------|--|
| A | A random sampling is always representative.   | false | <i>For particular analytical questions, a systematic sampling is required (e.g. specific time or position intervals).<sup>16</sup></i>                 |
| B | Chemicals for sample preparation can be a significant source for contamination.   | true  | <i>Any chemical used for sample preparation is a potential source of contamination due to impurities.</i>  |
| C | Contamination with a non-analyte substance during sample preparation <b>CANNOT</b> cause inaccuracies.                      | false | <i>Non-analyte substances alter the matrix and may lead to matrix effects or spectral interferences.</i>   |
| D | To evaluate the toxicity of fish filet based on organic arsenic compounds, a digestion with hydrogen peroxide is performed. | false | <i>Information on the mercury species is required, which are lost by the digestion. In this case, an extraction is more suitable than a digestion.</i> |

**7. General analytical chemistry.**

- |   |  |       |  |
|---|--|-------|--|
| A | The substance to be determined is termed analyte.  | true  | <i>by definition</i>   |
| B | During the sample preparation it is possible that the analyte is transformed into a different species. | true  | <i>For example, a change of oxidation state.</i>   |
| C | Non-analyte substances in a sample are termed "matrix".  | true  | <i>by definition</i>   |
| D | Interferences can only be caused by the sample matrix.   | false | <i>Other sources of interferences can be contaminations, reagents for sample preparation and originate from background signal such as plasma species in ICP-OES.</i> |

**8. Matrix effects...**

- |   |   |       |   |
|---|---|-------|---|
| A | ...lead to systematic errors.                                   | true  | <i>Matrix effects shift the measurement results in a particular direction and therefore cause for systematic errors.</i>  |
| B | ...CANNOT occur after a digestion.                              | false | <i>Even after digestions, matrix effects may occur, e.g., due to a high acid residue in the measurement solution.</i>   |
| C | ...can be taken into account with the standard addition method. | true  | <i>With standard addition, calibration is carried out matrix-matched.</i>   |
| D | ...can lead to underquantification.                             | true  | <i>Matrix effects may increase or decrease the slope of the calibration function. Increasing the slope, typically leads to an underquantification, e.g. a result lower than the actual analyte concentration.</i> |

**9. Lead is to be determined in glacial ice of the Himalaya. Which criteria need to be met by the analytical instrumentation for the measurement?**

- |   |                       |       |  |
|---|-----------------------|-------|--|
| A | Selectivity           | true  | <i>The selectivity for lead needs to be ensured, otherwise other elements or compounds will interfere.</i>   |
| B | Mobility              | false | <i>The sampling will need take place in the Himalaya, but the sample preparation and measurement can take place elsewhere as long as the sample is not altered in terms of the lead content (and distribution, as required).</i> |
| C | Small foot print      | false | <i>It is not necessarily required. If needed, large (heavy and expensive) equipment may be used.</i>   |
| D | Automation capability | false | <i>A matter of cost-benefit analysis, but automation is not always necessary.</i>  |

**10. You receive 30 L of a foul manure sample and determine heavy metals therein. You want to improve the precision. Which action is suitable?**

- |   |   |       |  |
|---|---|-------|--|
| A | Measure more aliquots.                                  | true  | <i>Repeated measurement improves the standard deviation and thereby the common measure of precision.</i> |
| B | Avoid spectral interferences.                           | false | <i>Spectral interferences do not (directly) influence precision.</i>                                     |
| C | Use standard addition for quantification.               | false | <i>Using standard addition does not influence precision of the result meaningfully.</i>                  |
| D | Thoroughly homogenize the sample the prior to analysis. | true  | <i>Thorough homogenization of the sample lead to more precise measurement results.</i>                   |

**11. You measure the Cu content in a bronze coin twice with the same method and get different results (0.5 µg/kg and 0.1 µg/kg). What are the possible causes?**

- |   |                                     |       |  |
|---|-------------------------------------|-------|--|
| A | Inhomogeneity                       | true  | <i>Inhomogeneity, even in liquid measurement samples due to omitted mixing after dilution, may cause inconsistent results.</i>   |
| B | Memory effects                      | true  | <i>Contamination from previous measurements, from a higher concentrated sample or standard, is a memory effect, which may cause higher signals in subsequent measurements.</i> |
| C | An unsuitable reference material    | false | <i>An unsuitable reference material or other standard may cause a systematic error due to unsuited calibration, but not inconsistencies for the same sample.</i>               |
| D | High uncertainty of the measurement | true  | <i>Some measurement techniques/analytical methods have a low precision.</i>  |

**12. You receive ten glass fragments of different origin and are asked to assign those to three reference glass samples on the basis of their element composition. Which actions are appropriate?**

- |   |  |       |   |
|---|--|-------|---|
| A | Analyze the ten fragments individually   | true  | <i>To determine the element composition of individual fragments, it is necessary to not mix the samples.</i>  |
| B | Sample digestion with HNO <sub>3</sub> and H <sub>2</sub> O <sub>2</sub> .             | false | <i>Glass cannot be digested with just HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>.</i>   |
| C | No need to worry about spectral interferences, since all samples have the same matrix. | false | <i>Spectral interferences may always occur. With the same matrix one may assume that similar, not necessarily the same and equally intensive, spectral interferences occur.</i> |
| D | Silicon may be added to all samples as an internal standard.                           | false | <i>Silicon is not added as an internal standard as it is already present in the sample.</i>   |

**13. A glass shard was digested with acid and cerium was determined in the resulting solution using external calibration. The results for the three solution aliquots differ significantly. What are possible causes?<sup>17</sup>**

- |   |  |       |   |
|---|--|-------|---|
| A | Unstable sample aspiration or nebulization     | true  | <i>This may lead to different results, e.g. different transport efficiencies for different aliquots.</i>                                    |
| B | Incomplete sample digestion                    | false | <i>The aliquots originate from the same solution.</i>   |
| C | Memory effects of previous cerium measurements | true  | <i>Memory effects can affect results of subsequent measurements. In this case higher values are expected for the first new measurement.</i> |
| D | Non-matrix matched calibration                 | false | <i>This would result in a systematic error and affect all measurements in the same manner.</i>  |

**14. At a border crossing point, customs officers seized a large box containing several thousand coins. There is suspicion that these coins are counterfeit. An analysis should clarify the case. Three coins were taken directly from the top surface.**

- |   |  |       |   |
|---|--|-------|---|
| A | Three coins are NOT representative for several thousand.   | true  | -   |
| B | Three coins are NOT enough material for a chemical digest. | false | <i>As a digest of a metal alloy and subsequent analysis for composition typically requires 1 g or less, three coins are sufficient.</i> |
| C | The coins should NOT only be taken from the top.           | true  | <i>Coins should be taken from different positions of the entire volume of the lot.</i>  |
| D | A non-destructive analysis is preferable.                  | true  | <i>...in case the coins are legit.</i>  |

## Atom Absorption and Emission Spectroscopy, Inductively Coupled Plasma Mass Spectrometry, and X-Ray Fluorescence Spectroscopy

**15. Methods<sup>18</sup>**

- |   |   |       |   |
|---|---|-------|---|
| A | ICP-OES and flame-AAS are absolute methods.                 | false | <i>ICP-OES and flame-AAS are relative methods and require calibration.</i>  |
| B | ETV-AAS is an absolute method.                              | false | <i>ETV-AAS is also a relative method and requires calibration.</i>  |
| C | Alkali effects only occur with ICP-OES, but not flame AAS.  | false | <i>The presence of alkali metals may have an influence on the ionization or excitation and thereby the absorbance of other elements. Example: Addition of Sr as ionization buffer for the determination of water hardness (Ca and Mg) by flame AAS.</i> |
| D | With ICP-OES it is possible to determine multiple analytes. | true  | <i>ICP-OES is a typical multi-element method. Simultaneous detection is possible with polychromators.</i>   |

**16. Method comparison**

- |   |   |       |   |
|---|---|-------|---|
| A | ETV (or graphite furnace)-AAS is better suited than flame AAS for fast screening of many samples. | false | <i>The different phases of a measurement with ETV-AAS increase the overall measurement time per sample substantially compared to flame AAS.</i>   |
| B | AAS is NOT a typical multi-element method.  | true  | <i>The common usage of hollow cathode lamps hinders multi-element analysis with AAS for routine measurements and also the introduction of continuum source (CS) AAS has not changed this.<sup>19</sup></i>          |
| C | The dynamic measurement range of ICP-OES is larger than for AAS.                                  | true  | <i>The typical range for AAS covers three decadic orders of magnitude, while this is five or six for ICP-OES, depending on the background intensity.</i>  |
| D | There are less spectral interferences with ICP-OES compared to AAS.                               | false | <i>Atom emission spectra are more prone to spectral interferences than atomic absorption spectra due to the multiple pathways of relaxation. In addition, there are more intense ion emission lines in ICP-OES.</i> |



### 17. Flames and plasmas in Analytical Chemistry

- A The element-specific emission of radiation from flames can be used for quantitative analysis. true *Yes, this is the principle of any emission spectroscopy.*
- B The ICP obtains its energy from the oxidation of argon. false *The energy is coupled into the plasma by induction. Oxidation of argon occurs, but does not provide energy to sustain the plasma.*
- C In ETV-AAS the analytes are evaporated in the furnace and excited in the flame. false *There is no flame in ETV-AAS. The furnace alone serves as the atomizer. Excitation of the analytes occurs due to absorption of element-specific radiation (often a hollow cathode lamp).*
- D There can be different charge states of the same element in a plasma. true *Uncharged element species can occur alongside single or multiple charge states of one element. They can be distinguished by their distinct emission lines.*

### 18. Features of element analytical methods

- A A simultaneous ICP-OES spectrometer allows the determination of aluminum in several samples at the same time. false *Simultaneous detection means detection of different wavelengths at the same time, not different samples. You need to introduce one sample at a time into the instrument/plasma.*
- B More efficient sample delivery systems can lead to lower limits of detection. true *More efficient sample delivery systems transport a larger portion of the sample into the system, thereby increase the sensitivity and hence lower the limit of detection (within the confines of other conditions and requirements).*
- C More efficient sample delivery systems decrease the matrix load. false *More efficient sample delivery systems transport a larger portion of the sample into the system, thereby increasing the matrix load.*
- D Single-element methods are more selective than multi-element methods. false *The selectivity is independent of the capability to detect multiple elements.*

### 19. Measurement and data analysis

- A Standard addition makes spectral interferences negligible. false *This is a typical misunderstanding. Standard addition circumvents non-spectral interferences (i.e. matrix effects, a multiplicative interference effect), but not spectral interferences.*
- B A micro-concentric nebulizer should be used with samples containing high levels of dissolved solids. false *These nebulizers offer low limits of detection, but are inclined to clog due to the small opening with larger matrix fractions.*
- C Glass sample introduction systems are NOT suitable for direct analysis of silicate rocks digested with HF. true *HF is incompatible with glassware. HF needs to be separated prior to measurements or another sample introduction system used (e.g. Teflon).*
- D Echelle spectrometers may allow for simultaneous detection of multiple analytes. true *Echelle spectrometers are polychromators. Opposite to monochromators with single detectors, simultaneous detection is possible with such polychromators.*

### 20. Atom spectroscopy

- A Quantitative analysis with flame AAS is based on the Lambert-Beer law. true *This is the principle of AAS.*
- B Quantitative analysis with ICP-OES is based on the absorption of radiation by elements. false *Quantifications with ICP-OES are based on the emission of radiation subsequent to thermal/collisional excitation.*
- C Excited analyte elements in flame AAS emit radiation to return to their ground state. true *Yes, although this is not utilized for detection, measurement, or quantification with flame-AAS.*
- D Continuum source (CS)-AAS instruments with xenon lamps allow for multi-element analyses. true *Continuum source (CS)-AAS instruments use a lamp with a broad emission spectrum, so effectively the entire range of UV/Vis wavelengths can be used for measurements. However, this requires a much more sophisticated spectrometer to isolate and measure the narrow atomic absorption lines.*

## 21. Atomic spectroscopy

- A AAS is based on the absorption of photons by ground-state atoms. true *This is a principle of AAS.*
- B ICP-OES is based on the emission of photons by ground-state atoms or ions. false *Atoms (and ions) need to first be excited to be able to emit element-specific radiation upon relaxation to be detected in ICP-OES.*
- C Flame AAS and ICP-OES require calibration. true *ICP-OES and F-AAS are relative methods and require calibration.*
- D The sample matrix affects the choice of the hollow cathode lamp for ETV-AAS analyses. false *The selection of the hollow cathode lamp depends on the analyte, i.e. from which element the cathode is made of.*

## 22. ETV-AAS is more sensitive than flame AAS because...

- A The dwell time of analytes in the beam path is longer. true *With flame AAS the dwell time in the flame is much shorter (stream of gas) compared to the furnace.*
- B The beam path in the graphite furnace is longer than in the flame. false *The beam path in the furnace (typically 3-5 cm) is shorter than in the flame (typically 5-15 cm).*
- C A larger sample volume is used for the graphite furnace. false *For graphite furnace less sample is used (typically 10-100  $\mu\text{L}$ ) compared to flame AAS (typically a few mL).*
- D There are no sample losses during the transport to the furnace. true *The sample is directly introduced into the furnace, while for the flame the solution is nebulized and only smaller droplets and a small sample portion reach the flame.*

## 23. You determine lead in limestone ( $\text{CaCO}_3$ ) by graphite furnace-AAS and use 10 mg aliquots without digestion of finely powdered sample for each measurement. Which standards can you use for matrix-matched calibration?

- A Lead salts dissolved in water in known concentration false *Water is not matrix-matched.*
- B Addition of calcium in known amounts to the sample aliquots. false *This cannot provide a calibration for lead.*
- C Addition of lead in known amounts to pure calcium carbonate. true *Pure calcium carbonate is a good match for limestone.*
- D Addition of lead in known amounts to the sample aliquots. true *This corresponds to the standard addition approach.*

## 24. The magnesium content was determined in two honey samples after digestion with conc. $\text{HNO}_3$ and $\text{H}_2\text{O}_2$ with flame AAS and external calibration. You want to assess the correctness of the results. Which is a suitable approach?

- A Using calcium as an internal standard. false *Whether a result is correct cannot be assessed with an internal standard.*
- B Addition of magnesium in a known amount to a sugar solution. true *This reference sample can be used to determine the recovery rate.*
- C Comparison of the magnesium content of both samples. false *Both samples may be affected by a same systematic error.*
- D Quantification of Mg in the honey samples with ICP-OES. true *Using another measurement technique is a good choice. Even better would be the utilization of a more direct measurement with a different sample preparation.*

## 25. You have already measured the external standards for calibration. Which of the following circumstances would result in analyte concentration values that are too high when measuring the samples with the flame AAS?

- A Additional emission due to matrix components at the measurement wavelength false *This spectral interference would lead to lower determined analyte values.*
- B Additional scattering of the hollow cathode lamp radiation due to particles in the flame. true *More scattering would lead to a decrease in measured intensity and therefore a higher analyte value.*
- C Increased nebulizer and transport efficiency true *Matrix effects, which lead to a larger amount of analyte within the beam path compared to calibration standards result in determining a higher analyte concentration.*
- D Increased hollow cathode lamp emission intensity false *The ratio between incident and emergent beam intensity is determined.*

**26. You determined copper in a copper solution using flame AAS. How can the sensitivity be increased?**

- A Increase the emission intensity of the hollow cathode lamp
- B Spike the reference solution with copper
- C Increase the length of the beam path in the flame
- D Use standard addition for calibration

- false *For quantification the ratio between incident and emergent beam intensity is used.*
- false *Altering the concentration in sample or reference solutions does not change the sensitivity of the measurement.*
- true *...according to the Lambert-Beer law.*
- false *Calibration using the standard addition method determines the sensitivity, and hence does not influence the sensitivity.*

**27. Which statements are true for analyses with ICP-OES?**

- A Uranium and thorium can be distinguished.
- B Silver isotopes can be distinguished.
- C Several different sample solutions can be measured automatically one after the other.
- D Tin can be detected selectively.

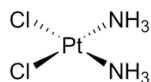
- true *Uranium and thorium are different elements and emit at different wavelengths.*
- false *The wavelength difference is very small, too small for routine ICP-OES instruments.*
- true *...using appropriate instrumentation such as autosamplers and software control.*
- true *Selectivity for a given analyte is a prerequisite for correct quantitative results.*

**28. A determination of cadmium using ICP-OES and standard addition leads to incorrect results. What are possible causes?**

- A Contamination during sample preparation.
- B Spectral interference
- C Ionization interference
- D Transport differences between sample and standard

- true *Sample contamination, here esp. with Cd, may cause incorrect results.*
- true *Even with standard addition, spectral interferences may cause incorrect results.*
- false *Ionization interferences are very unlikely when using standard addition for quantification since the conditions for both sample and standards the potential effects on ionization are the same.*
- false *Differences in sample transport do not occur with standard addition. (Special cases, such as clogging, are not considered.)*

**29. You have synthesized cisplatin. What information can you verify with ICP-OES?**



- A Oxidation state of platinum
- B Stoichiometric nitrogen content
- C Structure determination of the product
- D Synthesis yield

- false *ICP-OES is not suited to determine the oxidation state in this substance.*
- false *ICP-OES is not suited for nitrogen determinations.*
- false *With ICP-OES you cannot determine molecular structures.*
- false *ICP-OES cannot distinguish between the desired Pt compound and other Pt species.*

**30. Which statements are true for analyses with ICP-OES?**

- A The power coupled into an inductively coupled plasma influences the degree of ionization of the analytes.
- B Emission increases linearly with analyte concentration.
- C Temperature increases exponential with analyte concentration.
- D Spectral resolution increases with decreasing matrix concentration.

- true *The power influences the temperature and thereby the ionization of analytes.*
- true *This is the basis for quantification by ICP-OES (within the linear range).*
- false *There is no (direct) correlation of plasma temperature and analyte concentration. If there is, it may lead to deviations from the linear signal-concentration-relationship.*
- false *Spectral resolution is mainly a feature of the instrument's design and performance and not affected by the sample.*

**31. You aim to determine cadmium in an aqueous solution by ICP-OES. How do you select the measurement wavelengths for detection?**

- |   |   |       |  |
|---|---|-------|--|
| A | To achieve high sensitivity an emission line with high intensity is used.   | true  | <i>Sensitivity is the (change) of signal per unit of concentration (amount of analyte or mass fraction). Measurements on intensive (interference-free) wavelengths are more sensitive than less intensive wavelengths.</i> |
| B | To obtain correct results, an interference-free emission line is used.  | true  | <i>Spectral interferences result in incorrect analyses.</i>  |
| C | Cadmium is measured on the same wavelength used for the internal standard.  | false | <i>The internal standard is different from cadmium and therefore needs to be measured at a different wavelength.</i>   |
| D | Cadmium is measured on a different wavelength as the substance added for calibration by standard addition method. | false | <i>Standard addition means to add a known amount of analyte to the sample. Hence, the standard addition is measured on the same wavelength as the analyte.</i>   |

**32. What increases the spectral resolution of an ICP-OES instrument?**

- |   |   |       |   |
|---|---|-------|---|
| A | Smaller slits in the spectrometer.                    | true  | <i>As an example, the smaller the exit slit of the spectrometer, the smaller the range of wavelengths reaching the detector at a time.</i>  |
| B | Utilizing more than one detector.                     | false | <i>While utilizing more than one detector may shorten the amount of time required recording a spectrum and performing measurements, this has no influence on the spectral resolution. Keep in mind: most detector types cannot distinguish between different wavelengths.</i> |
| C | Measuring a more intense emission line of the analyte | false | <i>This only has an influence on the signal intensity, but not on the spectral resolution.</i>  |
| D | Repeated measurements of the sample.                  | false | <i>This only has an influence on the precision of the measurement, but not on the spectral resolution.</i>  |

**33. Which ions can be separated with an ICP-MS with a quadrupole mass analyzer [without collision/reaction cell]?**

- |   |  |       |   |
|---|--|-------|---|
| A | $^{40}\text{Ca}^+$ and $^{42}\text{Ca}^+$            | true  | <i>These isotopes result in signals at m/z 40 and 42, respectively. Those can, of course, be resolved by a quadrupole mass analyzer.</i>  |
| B | $^{40}\text{Ca}^+$ and $^{40}\text{Ar}^+$            | false | <i>Isobaric interferences cannot be resolved with a quadrupole mass analyzer.</i>   |
| C | $^{31}\text{P}^+$ and $^{62}\text{Ni}^{2+}$          | false | <i>The double charge on <math>^{62}\text{Ni}^{2+}</math> results in a signal at m/z 31, which cannot be resolved from <math>^{31}\text{P}^+</math> by a quadrupole mass analyzer.</i> |
| D | $^{31}\text{P}^+$ and $^{16}\text{O}^{15}\text{N}^+$ | false | <i><math>^{16}\text{O}^{15}\text{N}^+</math> results in a signal at m/z 31, which cannot be resolved from <math>^{31}\text{P}^+</math> by a quadrupole mass analyzer.</i>             |

**34. Which variables influence the sensitivity by ICP-MS?**

- |   |  |       |  |
|---|--|-------|--|
| A | The isotope selected for measurement   | true  | <i>Different isotopes have different abundancies and thereby show different sensitivities.</i>   |
| B | The ionization energy of the element   | true  | <i>The ionization energy affects the ionization rate of an element. A different ionization energy would lead to a different sensitivity.</i> |
| C | The number of measurements             | false | <i>The number of measurements has no influence on the sensitivity.</i>   |
| D | The oxide formation rate in the plasma | true  | <i>A high oxide formation rate results in less "unoxidized" ions and thereby affects the sensitivity.</i>                                    |

**35. ICP-MS and XRF**

- |   |  |       |   |
|---|--|-------|---|
| A | Matrix effects can occur with both measurement techniques. | true  | <i>Both ICP-MS and XRF are prone to matrix effects, e.g. ionization interference and secondary fluorescence, respectively.</i>        |
| B | ICP-MS has a higher sensitivity than XRF.                  | true  | -   |
| C | For XRF, the samples are bombarded with electrons.         | false | <i>While some x-ray sources may use bombardment of targets to generate x-rays, samples are irradiated with x-rays, not electrons.</i> |
| D | Both techniques can distinguish zinc and tin.              | true  | -   |

**36. What increases the spectral resolution of an ICP-MS instrument?**

- |   |   |       |  |
|---|---|-------|--|
| A | Smaller slits in a sector field instrument                  | true  | <i>As an example, the smaller the exit slit of the spectrometer, the smaller the range of wavelengths reaching the detector at a time.</i>   |
| B | Using a dual mode detector with analogue and pulse counting | false | <i>A dual mode detector increases the range (of ion beam intensity), but not the spectral resolution. Note: ICP-MS detectors themselves cannot distinguish between m/z values.</i> |
| C | Detection of barium at m/z 138 instead of 137.              | false | <i>While the resolution of an ICP-MS, depending on the can vary over the m/z range, the small difference between those isotopes is negligible for the resolution.</i>              |
| D | Increase the length of the quadrupole for an ICP-QMS        | true  | <i>The length of the quadrupole rods is indeed related to the resolution. However, longer rods decrease the transmission.</i>  |

**37. You are investigating crystals using XRF. What information can be obtained non-destructively?**

- |   |  |       |  |
|---|--|-------|--|
| A | Isotope composition                    | false | <i>Due to small differences in response, XRF is generally not suited for differentiation between isotopes.</i> |
| B | Determination of ultra-trace elements  | false | <i>XRF does not provide sufficient sensitivity for ultratrace element determination.</i>                       |
| C | Detection of inclusions of lithium     | false | <i>Like other light elements, lithium is not suited for detection by XRF.</i>                                  |
| D | Determination of the crystal structure | false | <i>Opposite to X-ray diffraction, XRF is not fit for the determination of crystal structures.</i>              |

## Scope of Element Analysis

The items below were developed for a particular course in quantitative instrumental element analysis. The methods covered included atomic absorption spectroscopy, atomic emission spectroscopy (i.e. inductively-coupled plasma optical emission spectroscopy), x-ray fluorescence spectroscopy and inductively coupled plasma mass spectrometry. Depending on the content of other courses, some statements/options may have different keys. They stem may be changed and specified accordingly. Each item below can be used for sets of four (kprime-type multiple-choice questions).

Can these tasks or questions be addressed directly with methods presented in this course?		Key	Explanation
1	Detection of iron in ancient ink on documents	true	-
2	Determination of the silicon in raw materials for high-performance alloys	true	-
3	Distinction between Chalcopyrite ( $\text{CuFeS}_2$ ) and Chalcocite ( $\text{Cu}_2\text{S}$ )	true	<i>The distinction is possible either qualitatively (presence of iron) or quantitatively (copper content).</i>
4	Determination of the calcium and magnesium content in honey	true	-
5	Determination of trace elements in a piece of jade jewelry	true	-
6	Differentiation between calcium oxide and calcium phosphate	true	<i>Differences in the calcium content allow distinction of the two compounds. Furthermore, although the techniques are not very sensitive to phosphorous, detection and quantification is possible.</i>
7	Confirmation of the origin of cacao based on trace element contents	true	<i>The trace element composition of cacao and similar products (e.g. coffee) are often cause by the soil in which it grows and therefore can provide valuable information on the origin.<sup>20</sup></i>
8	What is the emission of heavy metals from waste incineration?	true	-
9	Determination of lead in white wall paint	true	-
10	Quantification of silver in nanoparticles	true	-
11	How much calcium does the cappuccino contain?	true	-
12	Quantification of titanium dioxide nanoparticles in ketchup	true	-
13	Detection of cinnabar in paintings	true	<i>Cinnabar (mercury sulfide, <math>\text{HgS}</math>) is a mineral, which was used for a long time as red pigment.</i>
14	Determination of the heavy metal pollution due to a ship accident	true	-
15	Providing indication for which part of the motor does the abrasion particles in the old machine oil originate?	true	<i>Different parts are composed of different materials/alloys. The composition of abrasion particles can provide information on their origin.</i>
16	Determining the manufacturer of a car, based on glass shards after an accident.	true	<i>This is possible.<sup>21</sup> However, success seems less likely with newer models, as supply chains have changed and more similar compositions are used.</i>
17	Quantification of lithium in mobile phone batteries	true	-
18	Determination of the gold content in copper ore	true	-
19	Quantification of trace elements which serve as co-factors in a protein	true	-
20	What is the percentage of heavy metals removed from wastewater by a wastewater treatment plant?	true	-
21	Determination of the steel grade	true	-
22	Checking raw alloy material composition for compliance before further processing	true	-
23	Investigate the authenticity and composition of silver jewelry	true	<i>Trace elements in silver jewelry may provide information regarding its authenticity in conjunction with otherwise acquired information, e.g. comparison.</i>
24	Does taking a certain iron supplement change the blood iron level or by how much does the iron level improve?	true	-
25	How pure is the gold?	true	-
26	What metal is in that enzyme that I want to reproduce by total synthesis?	true	-
27	How much iron is actually contained in spinach?	true	-
28	Quantification of thallium in hair in suspected poisoning	true	-
29	How much silver is in silverfish?	true	-
30	Determination of the chemical formula of a metabolite.	false	<i>Metabolites are mostly organic compounds and do contain elements which are typically not detected with methods presented in this course.</i>
31	Quantification of phosgene residues in polymers	false	<i>Phosgene, <math>\text{COCl}_2</math>, does not contain elements which are typically detected with methods presented in this course.</i>
32	What is the oxalate content in spinach?	false	<i>Oxalate (from oxalic acid, <math>\text{C}_2\text{H}_2\text{O}_4</math>) does not contain elements which are typically detected with methods presented in this course.</i>

33	Determination of the acetylsalicylic acid content (aspirin) in pills	false	Acetylsalicylic acid, $C_9H_8O_4$ , is an organic component and <i>does not contain elements which are typically detected with methods presented in this course.</i>
34	Determination of the ammonium content in fertilizers	false	Ammonium, $NH_4^+$ , <i>does not contain elements which are typically detected with methods presented in this course.</i>
35	How high is the tolerable daily intake of lead?	false	<i>This is a question regarding toxicology, which cannot be approached with element analysis or analytical chemistry directly.</i>
36	How do silver nanoparticles affect bacteria?	false	<i>This question cannot be approached with element analysis directly and requires a much broader approach.</i>
37	How high is the tar content in cigarette smoke?	false	<i>Tar, a dark viscous liquid and a mixture of various hydrocarbons and free carbon, may result from pyrolysis of organic substances like tobacco, and does not contain elements which are typically detected with methods presented in this course.</i>
38	Quantification of amides in zwieback	false	<i>Amides, with the functional group <math>RC(=O)NR'R</math> (R are organic groups or hydrogen), do not contain elements which are typically detected with methods presented in this course.</i>
39	Determination of the oxygen content in blood	false	<i>Oxygen is typically not detected with methods presented in this course.</i>
40	How much zinc can be consumed daily without an elevated health risk?	false	<i>This is a question regarding toxicology, which cannot be approached with element analysis or analytical chemistry directly.</i>
41	How high is the content of carboxylic acids in butter?	false	<i>Carboxylic acids, with the functional group <math>RCOOH</math> (R is an organic group), do not contain elements which are typically detected with methods presented in this course.</i>
42	Toxicological investigation of pasta regarding acrylamide	false	<i>Acrylamide, <math>CH_2=CHC(O)NH_2</math>, is an organic compound and does not contain elements which are typically detected with methods presented in this course.</i>
43	Determination of the alcohol content in wine	false	<i>Alcohol (i.e. ethanol), <math>C_2H_5O</math>, is an organic compound and does not contain elements which are typically detected with methods presented in this course.</i>
44	Measurement of blood sugar	false	<i>Sugar is an organic compound and does not contain elements which are typically detected with methods presented in this course.</i>
45	Which wheat killers are in a jar of honey?	false	<i>Most wheat killers are organic compound and do not contain elements which are typically detected with methods presented in this course.</i>
46	Is the consumption of NaCl healthy?	false	<i>This is a question regarding impacts on health, which cannot be approached with element analysis or analytical chemistry directly.</i>
47	Determination of nitrate in vegetables.	false	<i>Nitrate is an anion, containing no elements suitable for detection with methods presented in this course.</i>
48	Determination of ozone pollution	false	<i>Ozone, <math>O_3</math>, is not an analyte determined with methods of this course.</i>
49	How much does the concentration of caffeine in the blood increase after drinking a coffee?	false	<i>Caffeine, <math>C_8H_{10}N_4O_2</math>, is an organic compound and does not contain elements which are typically detected with methods presented in this course.</i>
50	What are spider webs made of?	false	<i>Spider webs are made of organic compounds, which are not analyzed with methods presented in this course.</i>
51	How much microplastic does a jar of skin cream contain?	false	<i>Microplastic, i.e. polymer particles, are organic compounds and in general do not contain elements which are typically detected with methods presented in this course.</i>
52	Quantification of nitrogen oxides ( $NO_x$ ) in car and truck exhausts	false	<i><math>NO_x</math> are compounds which are not detected with methods presented in this course.</i>
53	How do $TiO_2$ nanoparticles affect aquatic organisms?	false	<i>This requires methods to investigate organisms.</i>
54	Influence of the sulfate content on the taste of water	false	<i>This requires methods to investigate taste and taste perception.</i>

## X-Ray Fluorescence Analysis

### XRF. Assess the following statements.

	Key	Explanation
1 XRF analyses are based on the Lambert-Beer law.	false	<i>The Lambert-Beer law describes the extinction of radiation intensity in methods of absorption spectroscopy. Although, absorption of radiation is involved in the process, XRF is a method of emission spectroscopy.</i>
2 The primary absorption results in excited ions.	true	<i>The primary absorption results in the removal of an electron of the inner shells of the atom and thereby to an ion, which is not in the ground state, i.e. excited.</i>
3 The fluorescence yield depends on the atomic number of the element.	true	<i>The extent of the fluorescence compared to competitive processes (e.g. Auger effect) depends on the atomic number of the elements. The larger the atomic number, the larger the fluorescence yield.</i>
4 $K_{\alpha}$ lines result from the detection of photoelectrons.	false	<i>Photoelectrons are those electrons, which are removed by the primary absorption of X-rays. <math>K_{\alpha}</math> lines result from fluorescence emission, which is released during the relaxation of the electrons from higher shells.</i>
5 For XRF, emitted electrons are measured.	false	<i>XRF detects (fluorescence) photons.</i>
6 The sample matrix has an influence on the information depth.	true	<i>The information depth is the sample depth from which 99% of the fluorescence radiation is absorbed. This depends on the permeability of the sample matrix.</i>
7 EDX instruments use different analyzer crystals to cover a larger range of the spectrum.	false	<i>EDX instruments do not contain analyzer crystals; the detectors themselves are sensitive to different photon energies.</i>
8 $K_{\alpha}$ lines are twice as intense as $K_{\beta}$ lines.	false	<i><math>K_{\alpha}</math> are about six times as intense as <math>K_{\beta}</math> lines.</i>
9 A longer wavelength corresponds to higher photon energy.	false	<i>A shorter wavelength corresponds to larger photon energy.</i>
10 In contrast to hydrogen, deuterium can be measured by XRF.	false	<i>As hydrogen, deuterium too only contains one electron and therefore does not show X-ray fluorescence.</i>
11 If an element is ionized by primary radiation and the atom relaxes under emission of radiation, this is termed secondary fluorescence.	false	<i>Secondary fluorescence is the process during which this fluorescence is absorbed by another atom, which in turn emits fluorescence.</i>
12 The absorption edge is the lowest energy required to result in the shell's ionization.	true	<i>by definition</i>
13 During EDX measurements the fluorescence lines are separated according to Bragg's law.	false	<i>EDX instruments do not contain analyzer crystals; the detectors themselves are sensitive to different wavelengths.</i>
14 Secondary fluorescence results from doubly excited atoms.	false	<i>Secondary fluorescence is the process during which the primary fluorescence is absorbed by another atom, which in turn emits fluorescence.</i>
15 For WDX, the position of the fluorescence lines on an energy scale is depending on the analyzer crystal.	false	<i>Opposite to the angle scale (<math>2\theta</math>), the position of the lines on energy is independent on the analyzer crystal.</i>
16 There are <b>NO</b> matrix effects for XRF analyses.	false	-
17 Quantification using XRF is <b>NOT</b> based on the Lambert-Beer law.	true	<i>The Lambert-Beer law describes the extinction of radiation intensity in methods of absorption spectroscopy. Although, absorption of radiation is involved in the process, XRF is a method of emission spectroscopy.</i>
18 Different elements do <b>NOT</b> absorb the same ratio of primary X-rays.	true	<i>The extent of the absorption depends on the atomic number.</i>
19 WDX is <b>NOT</b> a mobile method for on-site analyses.	true	<i>WDX involves large and rather immobile instrumentation.</i>



- <sup>1</sup> A good follow-up question could be „Under which circumstances would it make no difference?“ (When the cargo is homogeneous with respect to the distribution of the analyte(s)).
- <sup>2</sup> This question is related to a video case study, depicting the determination of cadmium in chocolate. Also note, that instead of option B (“water”) also “diluted acid” could also be used, which would be correct. See statements on “best option”.
- <sup>3</sup> “[Diluted] Acid” is not listed as an option. Cf. with the discussion of this question in main text of this paper. This question has been mentioned in context with peer instruction in Schwarz, G. Questions for Classroom Response Systems and Teaching Instrumental Element Analysis. *Chimia*, **2021**, *75*, 33-38; DOI: 10.2533/chimia.2021.33.
- <sup>4</sup> “Extraction” is not listed as an option. Cf. with the discussion of this question in main text of this paper.
- <sup>5</sup> This question and the challenge that students seem not to recognize that calibration by the standard addition method does not account for spectral interferences has been briefly discussed in Schwarz, G. Interface Model and Implementation Framework for Classroom Response Systems. *J. Chem. Educ.*, **2021**, *98*, 2122-2127; DOI: 10.1021/acs.jchemed.0c01339.
- <sup>6</sup> The context of this question is the determination of lead in children’s toys (wood or plastic) and refers to an analytical strategy developed during a lecture to digest and dilute samples.
- <sup>7</sup> Cammann, K. *Instrumentelle Analytische Chemie*, 1st ed.; Spektrum Akademischer Verlag: Berlin, **2001**, pp. 3-27.
- <sup>8</sup> This question relates to free atoms in the gas phase.
- <sup>9</sup> One to three distractors may be omitted for emphasis.
- <sup>10</sup> This question has been discussed in Schwarz, G. Interface Model and Implementation Framework for Classroom Response Systems. *J. Chem. Educ.*, **2021**, *98*, 2122-2127; DOI: 10.1021/acs.jchemed.0c01339.
- <sup>11</sup> A discussion of this question can be found in Schwarz, G. Questions for Classroom Response Systems and Teaching Instrumental Element Analysis. *Chimia*, **2021**, *75*, 33-38; DOI: 10.2533/chimia.2021.33.
- <sup>12</sup> Cf. with the discussion of this question in main text of the paper.
- <sup>13</sup> This question is related in part to the isotope table for ICP-MS used in the course. It contains the „element symbol” „Bg“ (i.e. background) for mass 220.
- <sup>14</sup> It may be reasonably argued that the question contains irrelevant information, i.e. on the isotope abundance of <sup>120</sup>Sn. However, please confer with the discussion in the maintext under “Writing and phrasing the question”. In addition, this question was used subsequent to a section on isotope dilution and as it was observed that students recalculated their results according to isotope abundancies in an ICPMS lab course experiment.
- <sup>15</sup> Krebs, K. The Swiss Way to Score Multiple True-False Items: Theoretical and Empirical Evidence. in: Scherpbier A.J.J.A.; van der Vleuten, C.P.M.; Rethans, J.J.; van der Steeg, A.F.W. (eds) *Advances in Medical Education*. Springer Netherlands, Dordrecht, **1997**, 158-161; DOI: 10.1007/978-94-011-4886-3\_46
- <sup>16</sup> Cf. Analytical Methods Committee, Random samples, *Anal. Methods*, **2014**, 2809-2811; DOI: 10.1039/C4AY90023E.
- <sup>17</sup> Cf. with a discussion and Tabel 1 in Schwarz, G. Questions for Classroom Response Systems and Teaching Instrumental Element Analysis. *Chimia*, **2021**, *75*, 33-38; DOI: 10.2533/chimia.2021.33.
- <sup>18</sup> For options A and B instead of “absolute method” the use of the term “primary methods” can be more appropriate.
- <sup>19</sup> Cf. Resano, M.; García-Ruiz, E.; Aramendía, M.; Belarra, M. A., Quo Vadis High-Resolution Continuum Source Atomic/Molecular Absorption Spectrometry?. *J. Anal. Atom. Spectrom.*, **2019**, *34*, 59; DOI: 10.1039/C8JA00256H
- <sup>20</sup> Cf. Bertoldi, D.; Barbero, A.; Camin, F.; Caligiani, A.; Larcher, R., Multielemental Fingerprinting and Geographic Traceability of Theobroma Cacao Beans and Cocoa Products. *Food Control*, **2016**, *46*, DOI: 10.1016/j.foodcont.2016.01.013
- <sup>21</sup> See for examples: Van Grieken, R.; Janssens, K.; Van Espen, P.; Injuk, J.; Padilla, R.; Vittiglio, G.; Potgieter, J. Novel Quantitative Procedures for In Situ X Ray Fluorescence Analysis. in: *In Situ Applications of X Ray Fluorescence Techniques*, IAEA (2005), p. 52. and Lee, S.-W.; Ryu, J.-S.; Min, J.-S.; Choi, M.-Y.; Lee, K.-S.; Shin, W.-J., Discrimination of Side-Window Glass of Korean Autos by Laser Ablation Inductively Coupled Plasma Mass Spectrometry. *Rapid Commun. Mass Sp.*, **2016**, *30*, 1612. DOI: 10.1002/rcm.7598.