Analysis of Heavy Metal Contaminants in Hemp and Tobacco Plant Using ICP-Mass Spectrometry

Uwe Oppermann[1], Johannes Hesper[1], Jan Knoop[1] [1]Shimadzu Europa GmbH, 47269 Duisburg, Germany

Figure 1: Cannabis/ hemp plants bioaccumulate metals in their tissues

1. Introduction

Plants and in particular tobacco plants, hemp tea leaves and flowers (a non-psychoactive species of cannabis) are well known to absorb trace elements from the soil and to accumulate them in their leaves. Some of these elements are toxic to human even in minute quantities. As they grow, plants can bioaccumulate metals in their tissues that originate from the soil and water in their surroundings. These metals can naturally occur in soils and water as part of their mineral content. They may also be artificially introduced in the form of fertilizers or crop protection products to increase the yields.

The emerging leader in metal analysis is ICP-MS because of its high sensitivity and high sample throughput resulting from quasi simultaneous multielement data acquisition. An argon plasma as ion source coupled with a rapid quadrupole for mass filtering are the main components of the system.

Here, we explore and discuss the applicability of the Shimadzu ICPMS-2030 to the detection of the "Big Four" heavy metals arsenic, cadmium, mercury, and lead (As, Cd, Hg, and Pb) and additionally beryllium, cobalt, chromium, nickel, and selenium (Be, Co, Cr, Ni, and Se) in a digested hemp flower (Sativa flowers) and two tobacco samples for compliance.

2. System Configuration

The Shimadzu ICPMS-2030 was used for analysis in combination with the Shimadzu AS-10 autosampler (Fig. 2). In-line addition of internal standards to calibration and unknown samples was accomplished using the Shimadzu Internal Standard Addition Kit. Based on the internal diameter of peristaltic tubing used for sample and internal standard injection, the approximate dilution of the internal standard solution was 90 %. High-purity reagents (Carl Roth GmbH, Germany) were used during sample preparation and dilution to ensure minimal contamination. Ultra-pure water (≥ 18.1 MΩ·cm; Sartorius, Germany) along with trace metal grade nitric acid was used for all dilutions and acidifications. All standards and unknown samples were prepared in cleaned single-use containers to minimize any cross-contamination between analytical runs. Thanks to the discrete dynode electro multiplier detector, ICPMS-2030 associates high sensitivity with a wide dynamic range (10^9) which is the key for simultaneous determination of major and trace elements. Due to the unique Eco-Mode with Minitorch, ICPMS-2030 is able to reduce running costs by half. The flat-octopole collision cell assures a high accuracy for all elements using Helium gas for Kinetic Energy Discrimination (KED) and suppresses spectroscopic interferences (poly atomic interferences). The efficiency of interferences suppression and enhancement of sensitivity are improved by a cooled cyclonic chamber and well controlled torch positioning.

Figure 2: Shimadzu inductively coupled plasma mass spectrometer ICPMS-2030 with AS-10 autosampler

3. Measuring Conditions

ICPMS-2030 can save all the masses from samples measurements and allowing results reprocessing without the need of new analysis. Thanks to its exclusive development assistant, LabSolutions ICPMS software is able to propose the optimum parameters for each element in the sample. Method development has never been easier and faster.

Parameter	Setting
RF generator power	1.2 kW
Plasma gas	8 L/min
Auxilliary gas	1,1 L/min
Carrier gas	0.7 L/min
Nebulizer type	Conical concentric
Sampling depth	5 mm
Spray Chamber temperature	5°C
Coll. Cell gas flow (He) DBG mode only	6 mL/min

Table 1: Operating conditions for Shimadzu ICPMS-2030

Operating conditions for the ICPMS-2030 are provided in Table 1 and analytical elements, selected masses, and internal standards in Table 2. Calibration curves were generated immediately prior to analysis to ensure the most accurate quantitation. The calibration curves (Fig.3) shown here on x-axis concentrations in µg/L and on y-axis internal standard corrected intensities (kcps).

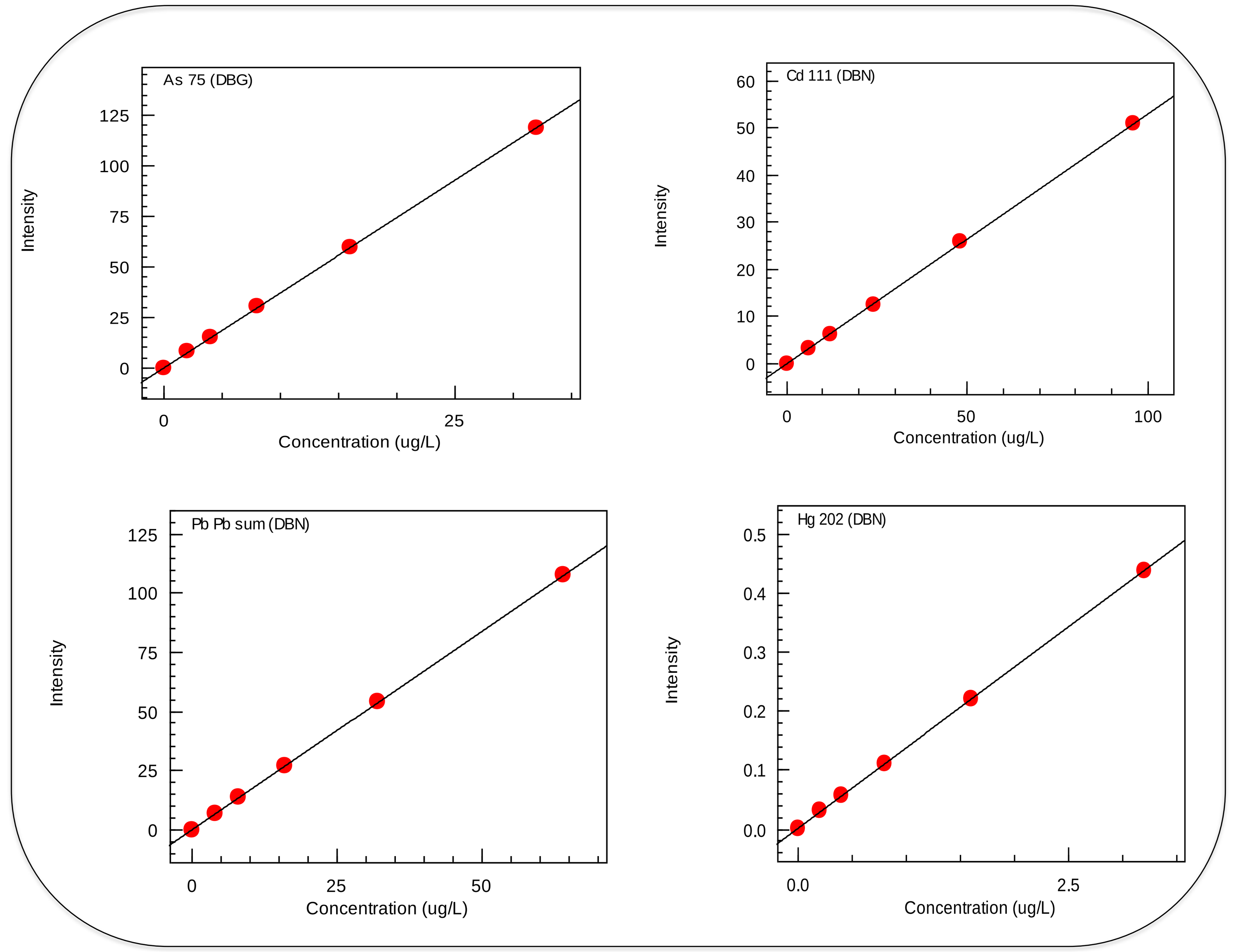

Figure 3: Calibration curves for As, Cd, Hg, and Pb

Element	Internal Std.
^{75}As	^{125}Te
^{9}Be	^{45}Sc
^{111}Cd	^{115}In
^{59}Co	^{103}Rh
^{52}Cr	^{103}Rh
^{202}Hg	^{205}Tl
^{60}Ni	^{103}Rh
^{78}Se	^{103}Rh
$^{206+207+208}$Pb	^{205}Tl

Table 2: Analytical elements, masses and internal standards

The Calibration curves in Figure 3 in the selected concentration ranges for each element demonstrated high linearity with a correlation coefficient r > 0.9998.

The recovery rates for the calibrated elements are between 89% (^{202}Hg) and 108% (^{52}Cr) as demonstrated in Figure 4.

4. Results

The recovery rates showing good accuracy of the method. But one more thing must be considered. The certified reference material, oriental basma tobacco leaves (INCT-OBTL-5) and virginia tobacco leaves (INCT-PVTL-6) which have been used for multielement trace analysis were also part of a study of 19 laboratories using ICPMS technology. Aim of that study (Proficiency test report, pub. Sep 2015) was to determine As, Be, Cd, Cr, Co, Ni, Pb and Se [1] in the above reference material.

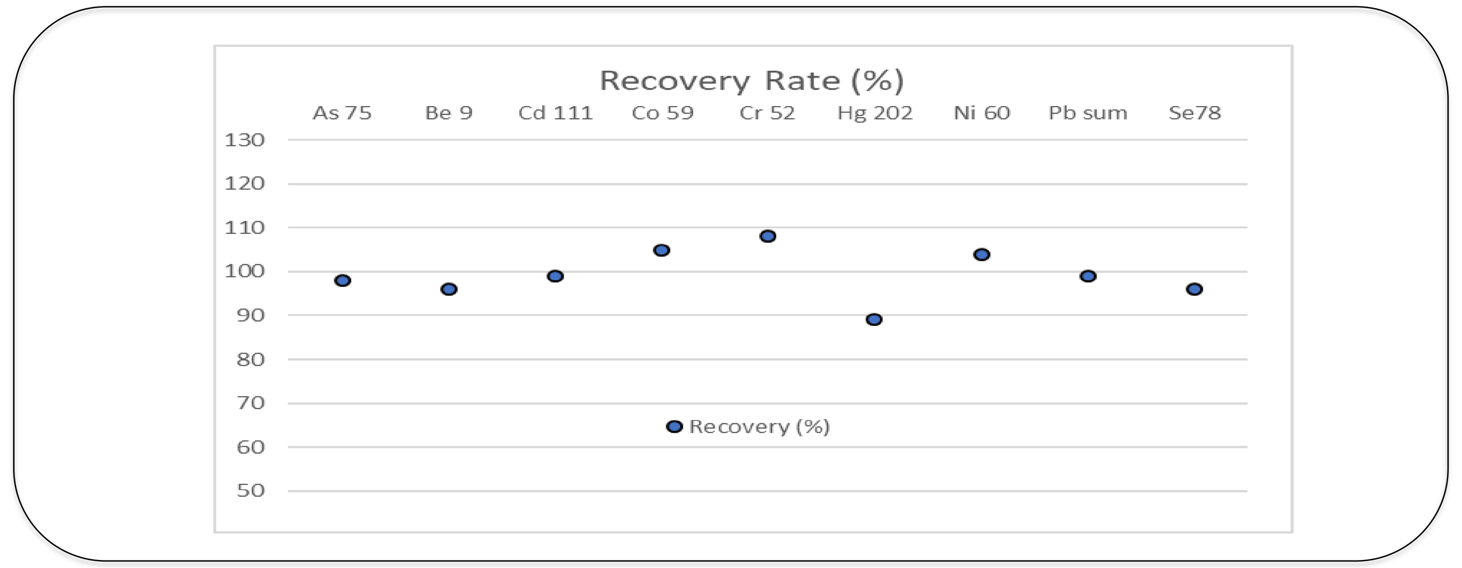

Figure 4: Recovery rates of calibrated elements

Some of the determined elemental concentrations (^{52}Cr, ^{78}Se, ^{202}Hg) differ much from the certified values or weren't re-analyzed (Hg). We found basically the same deviation. Therefore, for a better comparison with measured laboratory values, it was decided to use only for ^{202}Hg and for ^{78}Se the certified values. Hg was not part of the comparable study [1] and Se was differing too much in the study between 36+/-7 µg/L to 799+/-216 µg/L. Therefore, the certified Se value 88 ng/g was taken. All the other elements were compared using the average vales of the study. For more detail please see STS-CTR-Metals Proficiency Study – September 2015 [1].

The quantitative results are listed in Table 3 and demonstrate that the ICPMS-2030 is able to quantify simultaneously the various elements present in the reference samples.

Sample	^{75}As	^{9}Be	^{111}Cd	^{59}Co	^{52}Cr	^{202}Hg	^{60}Ni	^{sum}Pb	^{78}Se
Hemp A	113	44.3	46.5	201	1110	6.01	1360	397	54.9
Tobacco B	153	34.8	864	797	1500	16.3	2190	394	66.7
Tobacco C	304	84.5	836	395	1890	19.4	1420	1440	66.4

Table 3: Analytical results of hemp and tobacco samples in [µg/Kg]

5. Conclusion

Three samples were determined by inductively coupled plasma mass spectrometer ICPMS-2030 after microwave digestion: Hemp flower tea (Hemp A) and, two cigarette tobaccos (Tobacco B, and C). A method has been developed which is simple, fast, sensitive and accurate and a perfect fit for such type of plant material.

References

[1] Smokeless Tobacco Sub-Group, Proficiency Test Report, The Determination of As, Be, Cd, Cr, Co, Ni, Pb and Se in Reference Material, Sep. 2018, K. Wagner.