Efficiency of Modified Dry Decomposition for the Determination of Cr, Mo, Ni, and Ti in Plants*

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Received 16 October 2002

Efficiency of the different media for leaching of selected elements (Cr, Mo, Ni, Ti) from ash obtained by modified dry decomposition of plant materials in the presence of oxygen, ozone, and nitrous oxides using Dry Mode Mineralizer APION at 400 °C has been studied. Plant samples from IPE WEPAL interlaboratory exchange were used in the study. Data obtained for chromium, molybdenum, and nickel were evaluated by z-score classification using their contents calculated by test organizers as true values. Since the quality of Ti data given by IPE organizers is insufficient to be used for the evaluation with z-score attempt, Ti results determined after evaporation of ash with HF as total contents were used for the evaluation of the efficiency of ash dissolution. Risk of analyte losses δ by the retention in insoluble residues from decomposition of plant samples increases in the order $\delta(\mathrm{Cr}) \leq \delta(\mathrm{Mo}) < \delta(\mathrm{Ni}) < \delta(\mathrm{Ti})$.

Retention of analytes as Cd, Cr, Cu, Mn, Pb, and Zn in solid residue, which remains if soft leaching media are used after classical dry ashing, was often studied [1—4]. It is known that the retention strongly depends on decomposition temperature, *i.e.* it increases with elevated temperature. Here we present the data obtained for contents of chromium, molybdenum, nickel, and titanium in plants decomposed by modified dry ashing in the presence of oxygen, ozone, and nitrous oxides using Dry Mode Mineralizer APION (Tessek, CR), if different media were used for the dissolution of ash. Due to lower temperature of the decomposition in APION (400 °C) in comparison with classical dry ashing (500 °C), the risk of analyte losses could be decreased.

EXPERIMENTAL

Seven samples of internal or certified reference materials of plant origin differing in contents of the elements followed were used in this study (Table 1). Moreover, the samples differed in silica contents.

Concentration of chromium, molybdenum, nickel, and titanium in digests was measured by atomic spectroscopy with electrothermal atomization at following wavelengths: Cr – 357.9 nm, Mo – 313.3 nm, Ni – 232.0 nm, and Ti – 364.3 nm. The influence of matrix effects on signals was necessary to eliminate by standard addition calibration in case of Mo, Ni, and Ti.

Three modifications of the dissolution of ash obtained by the decomposition of the samples in the instrument APION were used:

A. Leaching with small amount of concentrated HNO_3 and dilution with 1.5 % HNO_3;

B. Leaching with small amount of *aqua regia* and dilution with 1.5 % HNO_3;

C. Evaporation of ash with the mixture of concentrated HNO_3 and HF to dryness, and dissolution of rest in small amount of *aqua regia* and dilution with 1.5 % HNO_3.

RESULTS AND DISCUSSION

z-Scores were applied for the evaluation of accuracy of the measured chromium, molybdenum, and nickel contents using the formula

$$Z = (Y - \mathrm{MED})/\mathrm{MAD}$$

if MED is median of IPE values, and MAD is median of absolute deviations in plant samples obtained from WEPAL IPE test, and

$$Z = (Y - X)/\sigma$$

if X is certified/recommended mean value, and σ half-width of the 95 % confidence interval of the mean X for certified reference material CRM 281 (rye grass). Employing the usual way of the z-score classification

*Presented at the XVIth Slovak Spectroscopic Conference, Košice, 23—27 June 2002.
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Table 1. Recommended/Certified Element Contents $w_{r,i}/(\text{mg kg}^{-1})$ in IRM IPE WEPAL Plant Materials and BCR CRM 281

Material	Origin	Values	Cr	Mo	Ni	Ti	Si
IPE 949	IPE	Median	0.487	0.530	0.420	2—23	1564
Aubergine	2001.2/2	MAD	0.083	0.038	0.047		24
IPE 683	IPE	Median	0.499	0.430	0.321	1.34—11.8	14540
Oat	2001.2/4	MAD	0.082	0.064	0.039		540
IPE 100	IPE	Median	1.771	1.561	1.456	31	10404
Grass (GR 94)	2001.3/2	MAD	0.137	0.075	0.046		804
IPE 149	IPE	Median	0.829	0.350	1.039	25.9	793
Lucerne 92	2001.3/1	MAD	0.186	0.050	0.063		327
IPE 883	IPE	Median	4.986	1.928	1.632	–	8873
Carnation	2002.1/1	MAD	0.320	0.125	0.119		
IPE 151	IPE	Median	4.270	2.397	3.400	111	7787
Grass (GR 95)	2001.3/4	MAD	1.000	0.162	0.350		222
CRM 281	BCR	Mean	2.100	0.840	3.000	8.4	–
Rye grass		Stand. dev.	0.400	0.060	0.170	0.7	

Table 2. Values of z-Scores for Cr, Mo, and Ni in Plant Materials Obtained if Dissolution Procedures A, B, and C of Ash were Applied

Material	Dissolution	Cr	Mo	Ni
IPE 949	*A*	−1.825	−0.015	−0.165
Aubergine	*B*	−0.291	2.705	0.097
	C	0.149	0.884	−0.941
IPE 683	*A*	−1.874	−0.273	−2.907
Oat	*B*	−1.229	0.616	−1.923
	C	0.254	−2.084	−1.279
IPE 100	*A*	−2.732	8.433	−8.206
Grass	*B*	−3.363	3.904	−1.876
	C	1.360	3.695	5.405
IPE 149	*A*	−1.452	0.117	−4.468
Lucerne	*B*	−0.285	0.468	1.900
	C	1.930	0.242	1.647
IPE 883	*A*	2.663	0.456	−2.430
Carnation	*B*	0.654	2.498	−2.939
	C	0.553	−0.803	5.336
IPE 151	*A*	−2.605	−1.480	−4.141
Grass	*B*	−0.448	0.629	2.697
	C	1.562	0.162	4.128
CRM 281	*A*	−1.614	−1.153	−5.262
Rye grass	*B*	−1.087	−0.844	−1.026
	C	0.396	4.400	2.492

as $|z| \leq 2$ – satisfactory, $2 < |z| < 3$ – questionable, and $|z| \geq 3$ unsatisfactory, we can see that some z-scores fall into the last category (Table 2).

Those are predominantly Ni contents found in the digests obtained after evaporation of ash with HF. Since laboratories participating in IPE interlaboratory test have been using decomposition with HF in limited extent only, median values derived by organizer of the test could be underestimated in comparison with true total nickel values. This suggestion can be confirmed by the fact that the most outlying values in our study have been determined in plants with high content of silica (grass 100, grass 151, carnation 883).

Quality of titanium data given by IPE organizers (Table 1) is insufficient to be used for the evaluation with z-score attempt. Ti results determined after evaporation of ash with HF as total contents were used for the evaluation of the efficiency of ash dissolution (Fig. 1).

Losses of Ti by retention in insoluble residue are 40—90 % depending on leaching agent and plant matrix. Since we are not able to distinguish which part of total titanium is bound in plant matrix, and which part could be given by possible contamination of material (*e.g.* milling in titanium mills, which could be used by organizer of the test), correlation between Ti values obtained after soft leaching (procedure A) and Si content in plants ($y_A = -0.001x_{Si} + 28.9$, $r = 0.48$) has only low predicating ability.

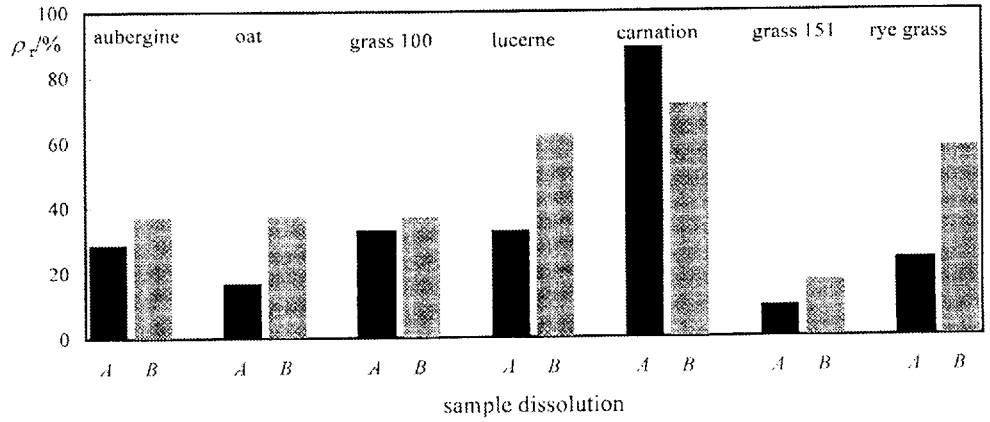

Fig. 1. Fractions of Ti ρ_r in digests obtained by procedures A and B from total Ti content obtained by procedure C.

Risk of analyte losses δ by the retention in insoluble residues from decomposition of plant samples by modified dry ashing in APION at 400 °C increases in the order $\delta(\mathrm{Cr}) \leq \delta(\mathrm{Mo}) < \delta(\mathrm{Ni}) \ll \delta(\mathrm{Ti})$.

Acknowledgements. This work was supported by the Grant MSM 412100004, Czech Ministry of Education.

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