

- 0.007, Zn²⁺ - 0.03, Ni²⁺ - 0.02, Mn²⁺ - 0.04, Pb²⁺ - 0.08, Fe²⁺ - 0.02.

Some rare earths (La³⁺, Ce³⁺, Pr³⁺ and Nd³⁺) were separated and determined with the use of an oxalic acid based eluent (80 mM oxalic acid + 150 mM LiOH), an Ion Pac CS5 column and the same

and Zn²⁺ were determined with the precision (relative standard deviation) better than 3% (Table).

On the basis of obtained results it can be concluded that the ion chromatograph Dionex 2000i/SP equipped with Ion Pac CS5 analytical column and the post-column reaction system allows the separation as

Table. Precision of chromatographic analysis of some transition cations in tap water sample.

Cation	Results of single determinations, x_i [mg·l ⁻¹]	Arithmetic mean, \bar{x} [mg·l ⁻¹]	Standard deviation, s [mg·l ⁻¹]	Relative standard deviation, s_r [%]
Fe ³⁺	0.125 0.127 0.121 0.126 0.129	0.126	0.006	2.38
Ni ²⁺	0.321 0.331 0.320 0.311 0.314	0.319	0.014	2.66
Zn ²⁺	1.19 1.21 1.16 1.22 1.20	1.196	0.023	1.92
Fe ²⁺	0.064 0.061 0.059 0.058 0.062	0.060	0.002	2.50

chromatographic system as for the transition metals. In aqueous solution, lanthanide metals are present as trivalent cations. The use of strong complexing agents such as oxalate results in the formation of anionic complexes of the lanthanide metals. Under these conditions, the lanthanide series may be separated by anion exchange mode. The chromatogram of separated La³⁺, Ce³⁺, Pr³⁺ and Nd³⁺ is presented in Fig.3. Estimated detection limits for the lanthanides were as follows (in ppm): La³⁺ - 0.18, Ce³⁺ - 0.16, Pr³⁺ - 0.34, Nd³⁺ - 0.07.

Analysis of the sample of tap water was performed and the obtained chromatogram is presented in Fig.4. The cations of Fe³⁺, Fe²⁺, Ni²⁺

well as accurate and precise determination of transition and lanthanide metals with low detection limits in aqueous samples.

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EFFECT OF THE SAMPLE MINERALIZATION METHOD ON THE ACCURACY OF Co DETERMINATION IN PLANT MATERIALS

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Many analytical methods for trace element determination, e.g. ICP/AES, GFAAS and electrochemical methods, require decomposition of the material to be analyzed. Great progress, which has been made in analytical instrumentation in the last two decades, has been not accompanied by the development of sample preparation methods. Hence, the sample preparation, when involved, has become the step of analysis, which may strongly affect the uncertainty of the final result. This is especially important in the determination of trace elements in plant materials, because plant materials are, as a rule, not homogeneous and usually contain various mineral fractions. The commonly used sample decomposition procedures do not always ensure com-

plete mineralization and may have an effect on both preconcentration and measurement steps. As an example the effect of mineralization procedure on analytical result was investigated during the determination of cobalt in plant materials. Cobalt is considered to be one of the so-called analytically difficult elements [1, 2]. Its content in biological materials is generally lower than 1 µg g⁻¹ [3-5].

The following methods of mineralization were investigated:

- classical open wet digestion procedures with nitric, perchloric and hydrofluoric acids;
- closed-vessel microwave digestion with nitric acid followed by open-vessel decomposition with perchloric and hydrofluoric acids;



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- closed-vessel microwave digestion with nitric, hydrofluoric acids and hydrogen peroxide. The studies were carried out using certified reference materials (CRMs) of plant origin, most of them certified for Co content. The cobalt content was determined using instrumental neutron activation analysis (INAA) and radiochemical neutron activation analysis (RNAA), because the nuclear properties of Co enable its determination by both INAA and RNAA methods with excellent detection limits (4 ng g^{-1} and 0.04 ng g^{-1} for INAA and RNAA, respectively). Previously elaborated in our Laboratory the "definitive" method for the determination of Co traces in biological materials was applied [6-9]. The combination of ion exchange and

were found. Hence, they can be considered equivalent. Good agreement of the results obtained by the RNAA method with the microwave digestion step and the non-destructive INAA results was found.

Losses of Co in the case of an incomplete decomposition are due to a failure in converting the analyte originally present in several chemical forms into a single form required for the applied procedure. In the case of a plant material two kinds of compounds, mineral and organic, must be taken into account. The mineral fraction originates mainly from soil and is characterized by a high Si content. This fraction is, as a rule, difficult to dissolve. For decomposition of mineral fraction and

Table. Results of Co determination by RNAA and INAA procedures.

Material	Certified or information value [ng g^{-1}]	RNAA results*			INAA results*
		open wet digestion**	microwave plus open digestion	microwave only digestion	
Virginia Tobacco Leaves CTA-VTL-2	429 ± 26	391 ± 15 n=15	425 ± 38 n=4	424 ± 6 n=4	420 ± 19 n=5
Tomato Leaves 1573a NIST	570 ± 20	490 ± 19 n=18	571 ± 32 n=7	570 ± 16 n=4	577 ± 23 n=4
Oriental Tobacco Leaves CTA-OTL-1	879 ± 39	906 ± 47 n=5	-	964 ± 17 n=14	967 ± 19 n=9
Bowen's Kale	63.2 ± 10.7	70.5 ± 8.9 n=9	-	-	71 ± 12 n=3
Spinach Leaves 1570a NIST	390 ± 50	363 ± 21 n=14	-	-	-
Hay Powder IAEA V-10	130 [110-140]	136 ± 5 n=9	-	-	141 ± 4 n=3
Orchard Leaves 1571 NBS	(200) ^{***} 160 ± 37 ^{****}	137 ± 7 n=10	-	148 ± 6 n=5	150 ± 22 n=4
Apple Leaves 1515 NIST	(90) ^{***}	81 ± 6 n=8	89 ± 13 n=2	92 ± 7 n=6	91 ± 11 n=6

* $\bar{x} \pm t_{0,05} \cdot s \cdot n^{-1/2}$.

** 10 ml of HNO_3 + 2 ml of HClO_4 + 10 ml of HF; sample mass 100-200 mg.

*** information value.

**** consensus value by Gladney et al. [10].

extraction chromatography used in this procedure assured a very selective and quantitative separation of ionic cobalt from all accompanying radionuclides present in acidic digest solution. In the case of incomplete decomposition of the sample, Co retained on the top of the first column could be detected using gamma ray spectrometry.

The results of Co determination are presented in Table. The results obtained by RNAA were compared with certified (or information) values and the results obtained by the INAA method by means of the Student's t-test. For some materials a distinct effect of the mineralization method on the results can be observed, i.e. statistically significant differences at 95% confidence level have been found between mean results. The materials affected are Virginia Tobacco Leaves CTA-VTL-2, Tomato Leaves NIST 1573a, Oriental Tobacco Leaves CTA-OTL-1, Apple Leaves NIST 1515 and also Orchard Leaves NBS 1571. The results obtained for open wet digestion are lower than those for two microwave decomposition methods. For the results obtained by the latter two methods no statistically significant differences at the 95% confidence level

volatilization of silica HF treatment has been included into the wet digestion procedures. The effectiveness of the decomposition depending on the amount of HF added has been examined in case of open wet digestion. The results are summarized in Fig. Taking into account the amount of HF necessary for complete mineralization the analyzed materials can be grouped into three categories: A - materials decomposed when 10 ml of HF were added (for 150 mg sample), B - required 15 ml of HF and C - materials for which even 15 ml of HF were not sufficiently effective. As follows from the above results (Fig.) the open wet decomposition with HNO_3 , HClO_4 and HF can be applied for some materials. However, for some plant materials (CTA-OTL-1, 1515 NIST) it is not sufficiently effective. The content of Si in the above CRMs was lower than 1%. So, in all the cases the amount of HF used significantly exceeded the stoichiometrically equivalent value. An increase in the HF amount up to 15 ml resulted in better recoveries of Co. However, the increase in the amount of HF requires also a longer time of decomposition, which might affect the Co recovery. It seems that the ne-

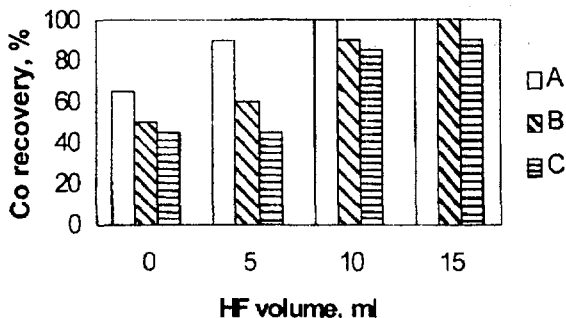


Fig. Co recovery as a function of HF amount used during open wet decomposition, sample mass ~150 mg, uncertainty of the results $\pm 5\%$. A - Bowen's Kale, Hay Powder IAEA V-10, Spinach Leaves NIST 1570a; B - Tomato Leaves NIST 1573a, Virginia Tobacco Leaves CTA-VTL-2, Orchard Leaves NBS 1571; C - Oriental Tobacco Leaves CTA-OTL-1, Apple Leaves NIST 1515.

gative systematic error could be also connected with the incomplete decomposition of organic compounds. It should be mentioned that the observed losses of Co depend on the gamma-radiation dose and temperature during irradiation. A higher dose and temperature result in more significant changes of organic matrix due to polymerization and dehydration and irradiated material is much more difficult for mineralization.

It follows from our results that the complete decomposition of all the investigated materials was reached when the closed-vessel microwave digestion with HNO_3 , H_2O_2 and HF was applied. This method reveals a number of advantages comparing

with the open wet decomposition. It takes much less time (1 h comparing with 8-16 h) and requires less reagents. It is easy to control and almost does not require supervision. Taking the above into account the use of the closed-vessel microwave decomposition should be recommended as a standard approach for plant materials.

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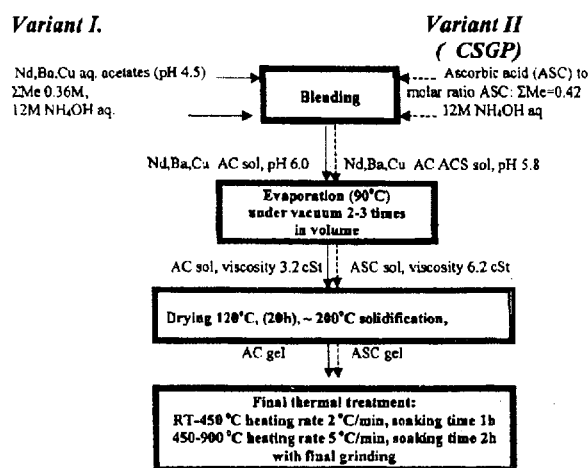
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SOL-GEL PROCESS FOR SYNTHESIS OF $\text{Nd}_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_x$ SUPERCONDUCTORS FROM Nd, Ba AND Cu ACETATES/AMMONIA/ASCORBIC ACID SYSTEMS

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The irreversibility line of $\text{NdBa}_2\text{Cu}_3\text{O}_x$ (Nd-123) superconductors is substantially above that of $\text{YBa}_2\text{Cu}_3\text{O}_x$ (Y-123) and much effort has been expended on fabricating Nd-123 materials [1-7]. In previous papers [8] we have described a new variant of sol-gel process to synthesize $\text{YBa}_2\text{Cu}_4\text{O}_8$ having satisfactory superconducting properties. This variant, Complex Sol-Gel Process (CSGP), utilizes ascorbic acid as a very strong complexing agent with strong reducing properties promoting formation of high phase purity in powders synthesized by sol-gel methods (INCT and ANL-USA teams patent [9]). The goal of this work was to synthesize a phase-pure nominal composition $\text{Nd}_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_x$ powder by the sol-gel method. We expect that this process can in the future be adapted to production of coated conductors. A further goal of this work was to compare Nd-123 powders made with and without ascorbic acid additions. A schematic diagram of the preparation of acetate (AC) and acetate-ascorbate (ASC) derived Nd-Ba cuprates is shown in Fig.1. The thermal analyses of AC and ASC dried



Irregularly shaped powders of $\text{Nd}_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_x$

Fig.1. Flow chart for preparation of irregularly shaped powders $\text{Nd}_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_x$ (derived from AC gel) and $\text{Nd}_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_x$ (derived from ASC gel).



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