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INSTRUMENTAL METHODS FOR ANALYSIS
OF SOME ELEMENTS IN FLOUR

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ABSTRACT

For ten various brands of flour contents of chosen (heavy) elements were determined by means of ICP, GF–AAS, PIXE and ASV/CSV methods. General performance of participating laboratories as well as pros and cons of different analytical methods were compared and discussed.

STRESZCZENIE

Dla dziesięciu gatunków mąki wykonano pomiary zawartości niektórych (ciężkich) pierwiastków za pomocą następujących metod: ICP, GF–AAS, PIXE, ASV/CSV. Przeprowadzono porównanie rzetelności pomiarów wykonanych przez różne laboratoria oraz zalet i wad użytych metod.

INTRODUCTION

Elemental trace analysis of organic materials is a challenge for modern analytical methods. Interlaboratory comparisons can reveal both the immanent shortcomings of different methods and the quality of performance. In the present work such comparison was carried out on samples of flour. Special attention was paid to problems connected with sample preparation prior to analysis which is the most important step in the analysis. Wet digestion, microwave digestion and no pretreatment of sample were compared.

EXPERIMENTAL

Methods of analysis

Metals levels were measured by atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), proton induced X-ray emission spectrometry (PIXE), and anodic/cathodic stripping voltammetry ASV/CSV).

Instrumentation

The CEM Corporation's Microwave Digestion System MDS-2000 was used for mineralization of samples prior to the analysis by AAS and ICP.

The atomic absorption analysis of Cd, Cu, Fe, Mn, Pb were performed with the Perkin-Elmer 5100 PC atomic absorption spectrometer equipped with the 5100 ZL Zeeman Furnace Module. The samples were injected into an integrated L'vov platform in the graphite furnace tube by means of AS-70 Furnace Autosampler. In Zn measurements the flame device of the Perkin-Elmer 5100 PC atomic absorption spectrometer was used (gas flows: C_2H_2 1.4 L min^{-1}, air 7.5 L min^{-1}). The instrument was fully computerized. Signals were recorded on a hard disk.

The ICP-Plasma 40 Perkin Elmer spectrometer was used for atomic emission studies. The spectrometer was connected with PC.

In the ASV/CSV methods the UPE-3 electrochemical analyser (Radius Cooperative, Gdańsk, Poland) was applied.

The beam source for PIXE analysis was the cyclotron C-48 at the INP.

Materials

Stock solutions of 1000 mg l^{-1} were obtained from the Polish Committee for Standardization of Measures and Quality Control. Analytic standard solutions were prepared from stock solutions by appropriate dilution with distilled water (4x). All solutions were stored in Nalgene polyethylene bottles. Certified reference wheat flour material (MP-1) was provided by the Laboratory of Radiometric Analyses (Institute of Physics and Nuclear Techniques, the Academy of Mining and Metallurgy, Cracow, Poland). Other reference material was obtained from the International Atomic Energy Agency (Vienna, Austria). The samples of flour were delivered by the Institute of Cultivation and Acclimatization of Plants, Cracow. They originated from various fields of the Plant Experimental Stations in Smolice and Oleśnica Mała.

Analysis by ICP-AES

The 0.5g samples were weighed into the digestion vessels and treated with 5.0 mL of nitric acid (Merck, Suprapur) , then inserted into the microwave digestion system. The

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processes of mineralization lasted about 25 minutes. After digestion the vessels were cooled to room temperature and the resulting solutions were diluted with water to a mass of ca. 50g. The main instrumental parameters for the analysis by ICP–AES were as follows: forward power 1.1 kW, plasma gas flow 15 L min^{-1}, auxiliary gas flow 1.1 L min^{-1}, nebulizer gas flow 2.5 L min^{-1}.

Analysis by GF–AAS

The 20 µl aliquots of resultant solutions (as described for ICP–AES) were dispensed automatically onto the tube and an optimized programme was run. In some cases the solutions were diluted several times according to the range of the calibration curve from which the concentrations of metals were calculated directly. Measurements were carried out in the absence of any chemical modifier. The temperature platform furnace conditions are shown in Table I.

Table I. GF–AAS Program's Parameter

Element	Ashing Temp.[°C]/Time [s]	Atomization Temp.[°C]/Time [s]
Cd	175/15	900/5
Cu	700/20	2100/2
Fe	1110/40	2000/5
Mn	1100/20	1900/5
Pb	450/20	1800/5

Analysis by PIXE

For PIXE analysis no pre–treatment was needed. The instrumental parameters for PIXE were as follows: 2.6 MeV proton beam, X–ray detector "ORTEC" – Si(Li) with detector active diameter of 6 mm, berylium window 0.0254 mm thick, resolution 200 eV FWHM at 5.9 keV ^{55}Fe, operating bias negative 1500 V, multichannel analyser ICA–70 coupled with a dedicated PC computer. The schematic view of the experimental arrangement was shown elsewhere [1].

Analysis by ASV/CSV

The wheat flour was dried at 60°C for 72 h. 500 mg samples were incubated overnight at room temperature with 4 ml of a mixture of 5 parts of HNO_3 and 1 part of $HClO_4$ (Merck), then mineralized by slow boiling and evaporation.. The dry inorganic matter was dissolved with 25 ml of redistilled and deionized water.

The measurements were performed with an impregnated stationary graphite electrode with a circular working surface and a calomel electrode as a reference. Mixing of the samples was carried out by a stream of nitrogen directed onto the surface of the graphite electrode.

Cadmium, lead and copper were analysed by anodic stripping, according to [2]. As a basic solution 0.5 M KCl was used, with the addition of 2×10^{-4} M $HgCl_2$ to improve evolution of metals on the working surface. The pre–electrolysis potential of −1.0 V was applied. The values of current density at the applied voltage of −0.63 V for cadmium, −0.43 V for lead and −0.03 V for copper were then recorded. The preconcentration time was established experimentally and was usually 3 – 10 min.

Manganese was analysed by cathodic stripping, according to [3]. The 0.5 M NH$_4$Cl + 0.5 M NH$_4$OH basic medium and +0.5 V pre–electrolysis potential were applied. The current density was recorded at the potential value of +0.3 V. The preconcentration time was 3–5 min.

All measurements were performed with standard addition technique. Each result represents an average of three separate measurements.

Quality control

The accuracy of the methods was tested by using certified materials MP–1 and V–8. A comparison of the experimentally determined values with the certified ones is listed in Table II and Table III.

Table II. Results for MP–1 Wheat Flour (ug g^{-1})

Analyte	Certified	AAS	ICP	PIXE	ASV/CSV
Cd	0.029±0.004	0.038±0.004	–	–	0.033±0.006
Cu	1.30±0.08	0.86±0.03	1.23±0.01	1.1±0.4	1.25±1.3
Fe	14.5±1.3	11.2±0.3	10.6±0.7	14.5±0.01	–
Mn	5.90±0.25	5.95±1.19	5.86±0.32	4.4±0.2	6.25±0.63
Zn	6.42±0.49	6.92±0.27	5.66±0.43	–	–

Table III. Results for V–8 Rye Flour (ug g^{-1})

Analyte	Certified	AAS	ICP	ASV/CSV
Cd	0.017	0.016±0.006	–	0.019 ± 0.003
Cu	0.95±0.19	0.85±0.07	0.98±0.16	1.00±0.12
Fe	4.1±0.7	3.7±0.3	3.5±0.1	–
Mn	2.06±0.12	2.00±0.13	2.13±0.04	3.07±0.52
Zn	2.53±0.33	2.31±0.14	2.05±0.09	–

RESULTS AND DISCUSSION

The summaries of results are shown in Tables IV–VII and in Figg. 1–6. The outliers were eliminated by Dixon's test. The confidence limits of the median were taken according to [4,5]. All results remaining after the elimination of outliers (with exception for the Zn result for sample No. 1) fulfilled the following conditions:
1. The relative uncertainty of the overall median does not exceed the limit: –50%; +60%.
2. The number of laboratory means rejected as outliers is no more than one.

The experiments indicate that with the use of any of the methods under study the measurements of Cu, Mn, Zn could be carried out successfully, with the sole exception of

ICP results for Cu levels, which had a positive bias [Fig. 2,4,6]. On the other hand, the analysis of Pb still remains the most difficult, which is often the case with Pb measurements in organic matrices [6]. Each method has its own limitations. On the PIXE spectrum the Pb peak was overlapped by the Kr peak. Unfortunately, there is no relevant reference material (flour) which contains the certified amount of

Pb. For these reasons the PIXE results could not be regarded as reliable. The ICP detection limit of Pb was of one magnitude higher than Pb content in working sample solutions. The signal given by the ASV method was sensitive to small changes in the conditions, esp. reagent contamination, so in this method the reagents of specific purity are needed; otherwise a substantial background error is introduced. The big characteristic mass of Pb is a disadvantage of GF-AAS. The last two methods gave the most reliable results for Cd content [Fig.1].

ACKNOWLEDGMENT

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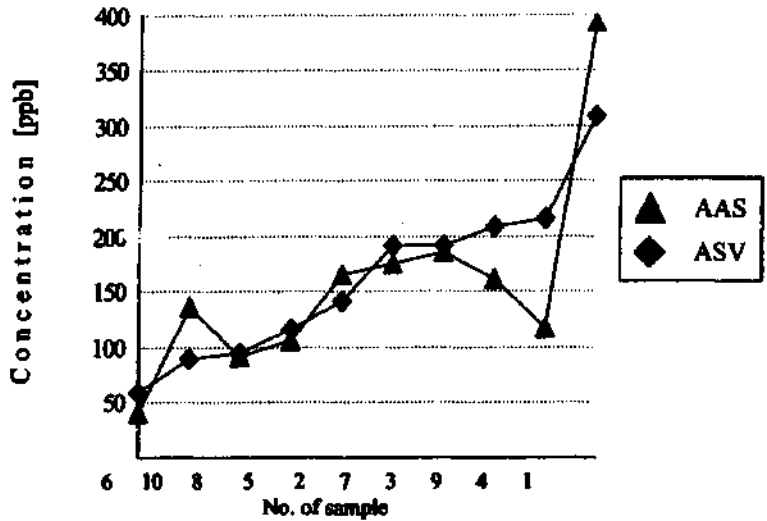
Fig. 1. Comparison between AAS and ASV/CSV results
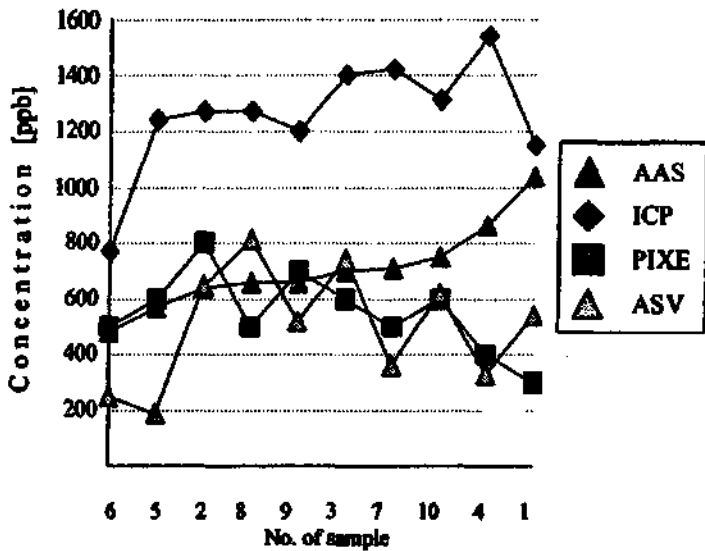for Cd measurements (results of ASV/CSV were chosen
as increasing values)

Fig. 2. Comparison between AAS, ICP, PIXE and ASV/CSV
results for Cu measurements (results of AAS were chosen
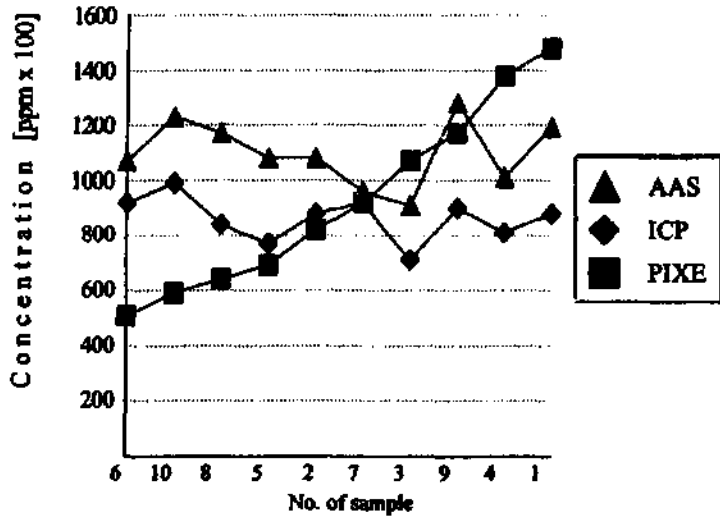as increasing values)

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Fig. 3.   Comparison between AAS, ICP and PIXE results
for Fe measurements (results of PIXE were chosen as
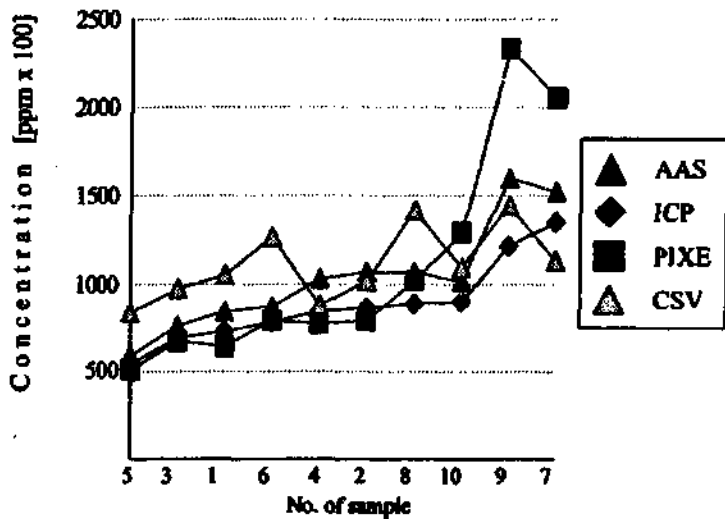increasing values)

Fig. 4.   Comparison between AAS, ICP and PIXE results
for Mn measurements (results of ICP were chosen as
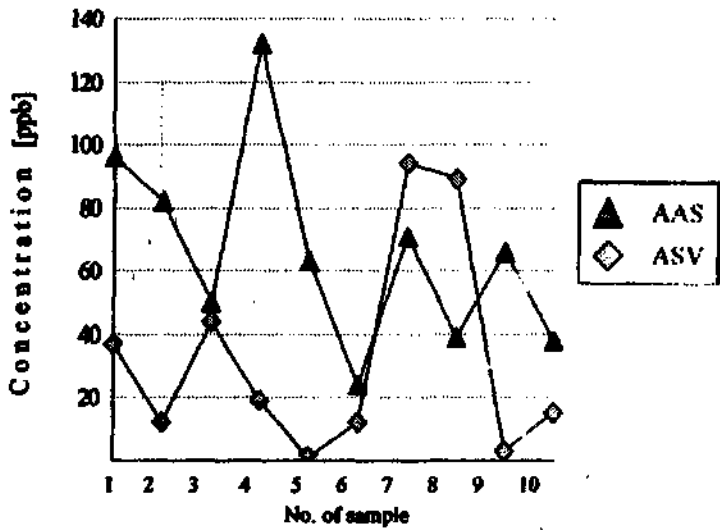increasing values)

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Fig. 5.   Comparison between AAS and ASV/CSV
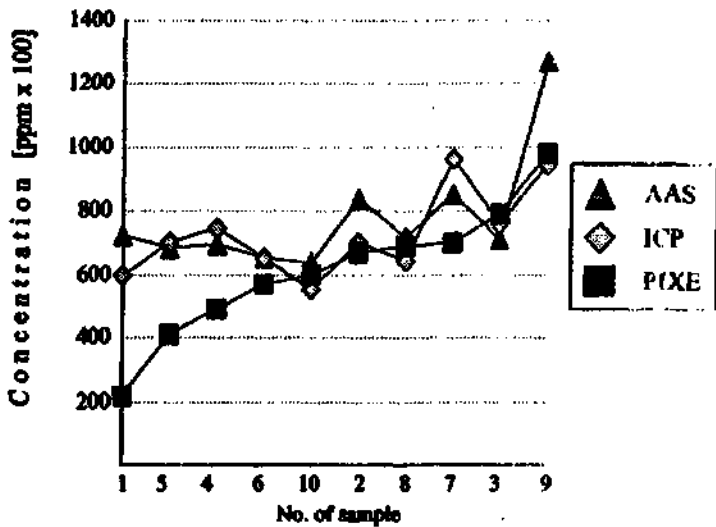results for Pb measurements.

Fig. 6.   Comparison between AAS, ICP and FIXE results
for Zn measurements (results of P:XE were chosen as
increasing values).

Table IV. Summary of Cu results.

Element determined Cu	No. of sample									
	1	2	3	4	5	6	7	8	9	10
No. of reported results	4	4	4	4	4	4	4	4	4	4
No of. accepted results	4	4	3	4	4	4	4	4	4	3
Total range of laboratory means	0.30÷1.50	0.64÷1.27	0.60÷1.40	0.33÷1.54	0.19÷1.24	0.25÷0.77	0.36÷1.42	0.50÷1.27	0.52÷1.20	0.60÷1.31
Range of accepted laboratory means	0.30÷1.50	0.64÷i.27	0.60÷0.74	0.33÷1.54	0.19÷1.24	0.25÷0.77	0.36÷1.42	0.50÷1.27	0.52÷1.20	0.60÷0.75
Overall mean of accepted laboratory means	0.76	0.84	0.68	0.78	0.65	0.50	0.75	0.81	0.77	0.66
Confidence limits of the overall mean at 0.05 sign.level	0.20+1.32	0.43+1.25	0.53÷0.82	0.02÷155	0.05÷1.25	0.21÷0.79	0.10÷1.40	0.35÷1.27	0.36÷1.18	0.49+0.82
Overall median of accepted laboratory means	0.79	0.73	0.72	0.63	0.59	0.49	0.61	0.74	0.68	0.69
Confidence limits of the overall median at 0.05 sign.level	0.54÷1.04	0.65÷0.8	0.70+0.74	0.4÷0.86	0.57+0.6	0.48÷0.5	0.5÷0.71	0.66÷0.81	0.66÷0.7	0.62÷0.75

Table V. Summary of Fe results.

Element determined Fe	No. of sample									
	1	2	3	4	5	6	7	8	9	10
No. of reported results	3	3	3	3	3	3	3	3	3	3
No. of accepted results	3	3	3	3	3	3	3	3	3	3
Total range of laboratory means	6.4÷11.7	8.8÷14.8	8.1÷13.8	8.2÷10.8	5.1÷10.7	9.2÷9.6	5.9÷12.3	6.9÷10.8	9.0÷12.8	7.1÷10.7
Range of accepted laboratory means	6.4÷11.7	8.8÷14.8	8.1÷13.8	8.2÷10.8	5.1÷10.7	9.2÷9.6	5.9÷12.3	6.9÷10.8	9.0÷12.8	7.1÷10.7
Overall mean of accepted laboratory means	8.8	11.8	10.7	9.3	8.3	9.5	9.4	8.5	11.2	9.0
Confidence limits of the overall mean at 0.05 sign. level	3.4÷14.3	5.8÷17.9	4.8÷6.5	6.5÷12.0	2.5÷14.2	9.0÷10.0	2.8÷15.9	4.3÷12.7	7.2÷15.1	5.3÷12.6
Overall median of accepted laboratory means	8.4	11.9	10.1	8.8	9.2	9.2	9.9	7.7	11.7	9.1

Table VI. Summary of Mn results.

Element determined Mn	No. of sample									
	1	2	3	4	5	6	7	8	9	10
No. of reported results	4	4	4	4	4	3	4	4	4	4
No of accepted results	4	4	3	4	4	4	4	4	4	3
Total range of laboratory means	6.4÷10.54	7.9÷10.71	6.7÷9.73	7.7÷10.29	5.1÷8.36	7.80÷12.6	11.34÷20.55	8.87÷14.1	12.15÷23.3	9.01÷12.9
Range of accepted laboratory means	6.4÷10.54	7.9÷10.71	6.7÷9.73	7.7÷10.29	5.1÷8.36	7.80+8.72	11.34÷20.55	8.87÷14.1	12.15÷23.3	9.01÷12.9
Overall mean of accepted laboratory means	8.2	9.4	7.7	8.8	6.2	8.2	15.2	11.0	16.5	10.8
Confidence limits of the overall mean at 0.05 sign. level	5.7÷10.6	7.6÷11.2	5.8÷9.6	7.3÷10.3	4.2+8.2	7.7+10.9	9.8+20.5	7.9+14.1	9.8÷23.1	9.2+12.4
Overall median of accepted laboratory means	7.83	9.4	7.23	8.60	5.65	8.3	14.35	10.4	15.19	10.56
Confidence limits of the overall median at 0.05 sign. level	7.25÷8.41	8.65÷10.1	6.88+7.58	8.42+8.78	5.42÷5.88	7.9+8.72	13.48÷15.22	10.2÷10.6	14.42÷15.97	10.17÷10.96

Table VII. Summary of Zn results.

Element determined Zn	No. of sample									
	1	2	3	4	5	6	7	8	9	10
No. of reported results	3	3	3	3	3	3	3	3	3	3
No of. accepted results	3	3	3	3	3	3	3	3	3	3
Total range of laboratory means	2.2÷7.24	6.7÷8.36	7.12÷7.9	4.9÷7.46	4.1÷7.03	5.7÷6.55	7.0÷9.63	6.44÷7.18	9.43÷12.66	5.54÷6.39
Range of accepted laboratory means	2.2÷7.24	6.7÷8.36	7.12÷7.9	4.9÷7.46	4.1÷7.03	5.7÷6.55	7.0÷9.63	6.44÷7.18	9.43÷12.66	5.54÷6.39
Overall mean of accepted laboratory means	5.1	7.4	7.5	6.4	6.0	6.3	8.4	6.8	10.6	6.0
Confidence limits of the overall mean at 0.05 sign. level	2.1÷8.2	5.6÷9.2	6.7÷8.3	3.7÷9.2	2.7÷7.3	5.3÷7.3	5.7÷11.1	6.1÷7.6	7.1÷14.2	5.1÷6.8
Overall median of accepted laboratory means	5.99	7.01	7.58	6.95	6.85	6.55	8.50	6.9	9.8	6.0