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Determination of plant-available micronutrients by the Mehlich 3 soil extractant – a proposal of critical values

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ABSTRACT

Soil testing in the Czech Republic is based on the use of the Mehlich 3 method for determination of macronutrients and diethylentriaminepentaacetic acid (DTPA) and hot-water extraction for determination of micronutrients. Since inductively coupled plasma optical emission spectrometers have become commonly used in soil testing laboratories, Mehlich 3 extractant could be used very effectively also for a simultaneous micronutrient determination. To take full advantage of the universal Mehlich 3 extractant, new criteria for evaluation of the content of micronutrients in this extractant are needed. The criteria presented in this study were obtained by a simple calculation of criteria from the relationships between the Mehlich 3 extractant and the extraction methods for which the criteria were available (DTPA for copper, zinc, manganese, iron and hot-water extraction for boron). The first calculated estimates of the criteria were pre-validated and slightly adjusted to minimize the difference between the frequency of the samples in each category after determination and evaluation by the compared methods. Further adjustment of the presented critical values with respect to the field and pot experiments will be necessary in the future.

Keywords: agriculture soil, extraction procedure, available microelements, result evaluation

The systematic soil testing scheme in the Czech Republic was established in 1961, founded on a long tradition of soil testing. A battery of traditional individual extractants (Egner P, Schachtschabel K, Schachtschabel Mg) was applied and the whole area of agriculture land was tested repeatedly in three-year periods. But after 30 years the increased economic pressures and substantial political and social changes opened the way also for a substantial change in the soil testing and Mehlich 2 (Mehlich 1978) universal soil extractant was adopted in 1991. Several years later, it was replaced by the improved and slightly modified method – Mehlich 3 (Mehlich 1984, Zbíral and Němec 2000). The Mehlich 3 extractant has been used since 1999 for determination of phosphorus (P), potassium (K), magnesium (Mg) and calcium (Ca). This universal soil extractant was chosen especially for its simple and universal use but also for its ability to produce relatively good correlations between the amount of nutrients extracted from the soil and the plant response. The Mehlich 3 extractant can be used for a multiple-element extraction from soils with a relatively wide pH range (with some limitations for carbonate soils) and it has a potential for a simultaneous determination of plant available nutrients, micronutrients (e.g. Mehlich 1984, Jones 1990, Ostatek-Boczynski and Lee-Steere 2012), sulphur (Zbíral 1999), index of phosphorus retention (Rayment and Lyons 2011) and also for determination of available fractions of some risk elements in soils (e.g. Minca et al. 2012, Čižmárová et al. 2016). Mehlich 3 extractant proved to be a suitable method for large-scale soil testing where high sample throughput is a crucial point. It is clear that in some special cases individual extracting procedures and a customized evaluation can give better fertilizer recommendation, but for a large-scale soil survey of highly varied soils Mehlich 3 was found to be a very good choice.

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Mehlich 3 extractant has been studied, modified and recommended by numerous authors (e.g. Wolf and Baker 1985, Sims 1989, Mateovič and Duráčková 1994, Wendt 1995, Eckert and Watson 1996, Zbíral and Němec 1999, 2000) and it is now a widely recommended and applied extracting procedure. Critical values in the Czech soil testing scheme were recalculated for P, K, Mg and Ca from the values established for the formerly used traditional extractants using the relationships between these extractants and Mehlich 3 (Zbíral et al. 2001). The criteria were further confirmed and adjusted using the results from the long-term field and pot experiments covering practically all soil and climate conditions of the Czech Republic and representing all major crops (Trávník et al. 1999).

Determination of plant available micronutrients was also included into the soil testing scheme but was provided only in special cases. Diethylentriaminepentaacetic acid (DTPA) extraction procedure developed by Norvell and Lindsay (1978) was used for determination of copper (Cu), zinc (Zn), iron (Fe) and manganese (Mn). Boron (B) was determined after hot-water extraction (Berger and Truog 1939). The methods were chosen because they were widely used and the DTPA method was available as an international standard (ISO 14870, 2001). But the methods do not meet all requirements for a time- and cost-effective procedure. Therefore relationships between the Mehlich 3 extractant and the extractants for determination of micronutrients were studied (Zbíral and Němec 1998, 2000, 2009) to find a possibility to widen the Mehlich 3 scope also for micronutrient determination. It was proved that Mehlich 3 could be used also for determination of B, Cu, Zn, Mn and Fe if the criteria for evaluation of the results are available. Any universal soil extractant can be used effectively only if a fast, cheap and reliable method of analysis is available (Jones 1990). Inductively-coupled plasma optical emission spectrometry (ICP-OES) was found to be the best choice for analysis of Mehlich 3 extracts mainly due to the ability of the method to determine all nutrients (including sulphur) and micronutrients simultaneously in one analytical step. The advantage of the method is also in a wide linear concentration range for all elements, adequate sensitivity and low or well-known interferences (Zbíral 2000). ICP-OES is nowadays routinely used in soil testing laboratories and therefore these laboratories could take full advantage of the multielement potential of Mehlich 3 universal soil extractant.

It has been mentioned that suitable and reliable criteria for fertilizer recommendation for Mehlich 3 extractant in the Czech soil testing scheme were established only for K, Mg, Ca and P. The goal of this study was to propose new criteria for Mehlich 3 extractable copper, zinc, iron, manganese, and boron measured by direct aspiration of soil extracts into the ICP-OES instrument simultaneously with the measurement of P, K, Mg and Ca.

METHODS

Samples. The same procedure for sample pretreatment as for the samples in the regular soil

Table 1. Descriptive statistics of soil sample sets. 95 soil samples (Cu, Zn, Mn, Fe) and 147 soil samples (B) (mg/kg)

Element	Method	AM	MED	MIN	MAX	LQ	UQ
Cu	DTPA	2.11	1.60	0.45	16.0	1.14	2.21
	M3	3.55	2.80	0.50	30.0	1.93	3.75
Zn	DTPA	3.47	2.13	0.65	87.7	1.50	3.13
	M3	6.73	4.17	1.50	147	3.20	5.55
Mn	DTPA	48.4	44.1	7.53	144	26.8	61.7
	M3	126	117	13.7	384	93.0	155
Fe	DTPA	73.4	59.8	8.7	453	32.6	87.3
	M3	372	378	73.3	1882	269	437
B	HW	0.83	0.58	0.08	2.70	0.39	1.14
	M3	0.87	0.74	0.22	3.23	0.50	1.06

AM – arithmetical mean; MED – median; MIN – minimum value; MAX – maximum value; LQ – lower quartile; UQ – upper quartile; DTPA – extraction by DTPA; HW – hot-water extraction; M3 – Mehlich 3 extraction

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Table 2. Soil extractants. Extraction ratios and times. Numbers in parentheses are concentrations (mol/L)

Method	Mehlich 3	DTPA	Hot-water extraction
	CH_3COOH (0.20) NH_4F (0.015) HNO_3 (0.013) NH_4NO_3 (0.25) EDTA (0.001)	triethanolamine(0.1) $CaCl_2$(0.01) DTPA(0.005) NH_4Cl(0.20)	deionized water, boron-free
Sample (g)	10	10	10
Extraction time (min)	10	120	5 min boiling
Soil:extractant ratio (g:mL)	1:10	1:2	1:5
References	Mehlich (1984)	Norvell and Lindsay (1972, ISO 14870, 2001)	Berger and Truog (1939)

testing was used. Soil samples were air dried and a fraction under 2 mm diameter was used for analysis.

For the comparison of the DTPA and Mehlich 3 extractants, 95 soil samples from soil monitoring plots were collected (Zbíral and Němec 1998). Agriculture topsoil samples (147 individual samples) from arable land were collected for the boron hot-water extraction and Mehlich 3 comparison (Zbíral and Němec 2009). Soil samples in both data sets represented all major soil types, climatic regions and proportions of agronomic cultures in the Czech Republic. Descriptive statistics of the samples are given in Table 1. Extraction methods are described in Table 2.

All reagents and standard solutions were prepared using Milli Q deionized water (Millipore, Bedford, USA). All chemicals were either from Fluka (Fluka Chemie AG, Buchs, Switzerland) or Merck (Merck KGaG, Darmstadt, Germany). Calibrating solutions were prepared by diluting commercially available certified standard solutions 1000 mg/L (Analytika, Prague). Plastic glassware was used to avoid contamination by boron.

All elements were determined by ICP-OES using IRIS INTREPID (Thermo Elemental, Madison, USA). The calibration curves were linear in the whole concentration range. Sample flow was 2.40 mL/min, RF 1150 W, nebulizer gas flow 0.55 L/min, auxiliary gas 0.5 L/min. Signal was integrated for 5–20 s and corrected for a background signal. The following emission lines were used for the measurement: B 249,773 nm, Zn 213.856 nm, Mn 257.610 nm, Fe 259.940 nm, and Cu 324.754 nm.

Excel (Microsoft, Redmond, USA), NCSS 2001 (NCSS, Kaysville, USA) and Statistica 6.0 (Statsoft, Tulsa, USA) computer program packages were used for statistical evaluation.

RESULTS AND DISCUSSION

From Table 1 we can conclude that Mehlich 3 was more efficient than DTPA or hot water in extracting the studied micronutrients. Mehlich 3 extracted about 50–80% more copper and zinc, 100–150% more manganese and 6–10 times more iron than DTPA. If compared with hot-water extraction Mehlich 3 was about 10–15% more efficient. The concentration of all elements in the Mehlich 3 extractant was high enough for a direct determination by ICP-OES. From the regression analysis of the results for the DTPA and Mehlich 3 methods (Table 3) can be seen that the correlation for copper and zinc was very good and the calculation of the criteria was relatively reliable. The correlation for Mn and Fe was also acceptable for calculation of the criteria. The relationship between hot-water extractable boron and Mehlich 3 extractable boron was also highly significant and

Table 3. Results of regression analysis. Single linear model M3 = a + bDTPA (HW)

Element	*a*	*b*	*R*	Significance
Cu	0.2085	1.585	0.928	++
Zn	0.8784	1.685	0.984	++
Mn	78.944	0.972	0.532	++
Fe	179.76	2.619	0.842	++
B	0.1707	1.1829	0.890	++

a – intercept; *b* – slope; *R* – correlation coefficient; ++ – highly significant at the 99% level; M3 – Mehlich 3 extractant; DTPA – diethylentriaminepentaacetic acid extractant; HW – extraction of boron by hot water

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Table 4. Frequency of samples in each category after evaluation according to the proposed Mehlich 3 criteria (Table 5) and DTPA or hot-water criteria (Table 6)

Category	Cu		Zn		Mn		Fe		B	
	DTPA	M3	DTPA	M3	DTPA	M3	DTPA	M3	HW	M3
Low	14	14	8	8	3	4	0	0	74	67
Medium	65	69	52	51	84	84	63	64	31	39
High	16	12	35	36	8	7	32	31	42	41

DTPA – extraction by diethylentriaminepentaacetic acid; M3 – extraction by Mehlich 3; HW – extraction by hot water

the regression equation could be used for the first estimate of the criteria calculation.

The detailed description of the relationships can be found in the published articles (Zbíral and Němec 1998, 2009). The relationships summarized in Table 3 were used for calculation of the criteria for Mehlich 3 extractant. The calculated estimates of the criteria were slightly adjusted to minimize the differences between the frequency of samples in each category (high, medium, low) after evaluation according to the former (DTPA, hot water) and to the proposed (Mehlich 3) criteria. From the results summarized in Table 4 can be concluded that the distribution of the samples into the categories for Mehlich 3 and DTPA extractants was practically identical for zinc, manganese and iron. There was a slight shift of the values from the category high to the category medium for copper and from the category low to the category medium for boron. However, the differences were small and the criteria presented in Table 5 can be accepted as the best first estimate of criteria for the Mehlich 3 extractant. The criteria published by Juráni et al. (1990) for DTPA and hot-water extraction are given in Table 6 for comparison.

In conclusion, the available data were used to calculate the criteria for boron, copper, zinc, manganese and iron determined after Mehlich 3 extraction and ICP-OES determination. The criteria were derived from the values published by Juráni (1990). The new criteria presented in this study are only the first estimate obtained by a simple calculation of criteria from the relationships between the Mehlich 3 extractant and the extraction methods for which the criteria were published. It must be stressed that this first estimate of the criteria should be improved for individual crops and soils with respect to the field and pot experiments.

Table 5. Proposal of criteria for Cu, Zn, Mn, Fe and B extracted by Mehlich 3 and determined by ICP-OES

Micro-nutrient	Soil type	Content (mg/kg)		
		low	medium	high
B	light soils	< 0.55	0.56–0.75	> 0.75
	medium soils	< 0.70	0.71–1.00	> 1.00
	heavy soils	< 0.85	0.86–1.40	> 1.40
Cu		< 1.6 (< 2.0)[1]	1.61–4.5	> 4.5
Zn		< 2.2	2.21–5.0	> 5.0
Mn		< 30 (< 45.0)[2]	30.1–200	> 200
Fe		< 60.0	60.0–420	> 420

[1] Recommended for cereal crops; [2] It is recommended to use fertilizers for soils with less than 45 mg/kg

Table 6. Criteria for Cu, Zn, Mn and Fe extracted by DTPA and hot-water extractable B (Juráni 1990)

Micro-nutrient	Soil type	Content (mg/kg)		
		low	medium	high
B	light soils	< 0.40	0.40–0.70	> 0.70
	medium soils	< 0.60	0.60–1.00	> 1.00
	heavy soils	< 0.80	0.80–1.50	> 1.50
Cu		< 0.80 (< 1.0)[1]	0.80–2.7	> 2.7
Zn		< 1.0	1.0–2.5	> 2.5
Mn		< 10.0 (< 15.0)[2]	10.0–100	> 100
Fe		< 8.0	8.0–75	> 75

[1] Recommended for cereal crops; [2] It is recommended to use fertilizers for soils with less than 15 mg/kg

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