Expanded measurement uncertainties of single- and group-specific methods

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Introduction

In the last years a number of single- and group-specific methods (SRM) were established for analysing parameters like chlorate, phosphonic acid, etc. The single- and group-specific methods focus on a limited number of parameters with similar chemical and physical properties. As opposed to that, the multi-residue approach is a compromise between the number of pesticides included and the suitability of the applied protocols for identification and optimal quantification of the individual pesticide.

A default expanded measurement uncertainty (exp. MU) of 50 % was derived from EU proficiency tests for multi-residue methods [1]. As a consequence, intralaboratory exp. MUs of at least <50 % are requested by accreditation bodies (validation data) and an exp. MU of 50 % is applied in case of MRL-exceedance [1].

Whether or not an expanded measurement uncertainty of 50 % is appropriate for single- and group specific methods is examined in the presented work by evaluating data of current proficiency tests.

Method

28 proficiency tests (2012 to 2016) organised by Bipea, EU-RL, FAPAS and PROOF-ACS are selected for evaluation. The selection is based on the parameters included and on the availability of the test reports to the authors (see table and references for details).

The proficiency tests cover the parameters chlorate, chlormequat, cyromazine, ethephon, glyphosate, maleic hydrazide, mepiquat, nicotine, perchlorate, phosphonic acid, and quaternary ammonium compounds (QAC). SRM of labile analytes like dithianon and dithiocarbamates are not considered. Matrices are fruits and vegetables, cereals, tea, dairy products and eggs.

The evaluation is performed similar to the approach applied for multi-residue methods in the past. The exp. MU is derived of the robust standard deviation $\hat{\sigma}$, the assigned value $\hat{X}$ and a coverage factor of 2 for a confidence level of 95 % [2]:

$$\exp MU\,[\%] = \frac{\hat{\sigma}}{\hat{X}} \times 100 \times 2$$

Each parameter in each proficiency test is evaluated separately. Thereafter, mean values of the exp. MUs are calculated for each parameter.

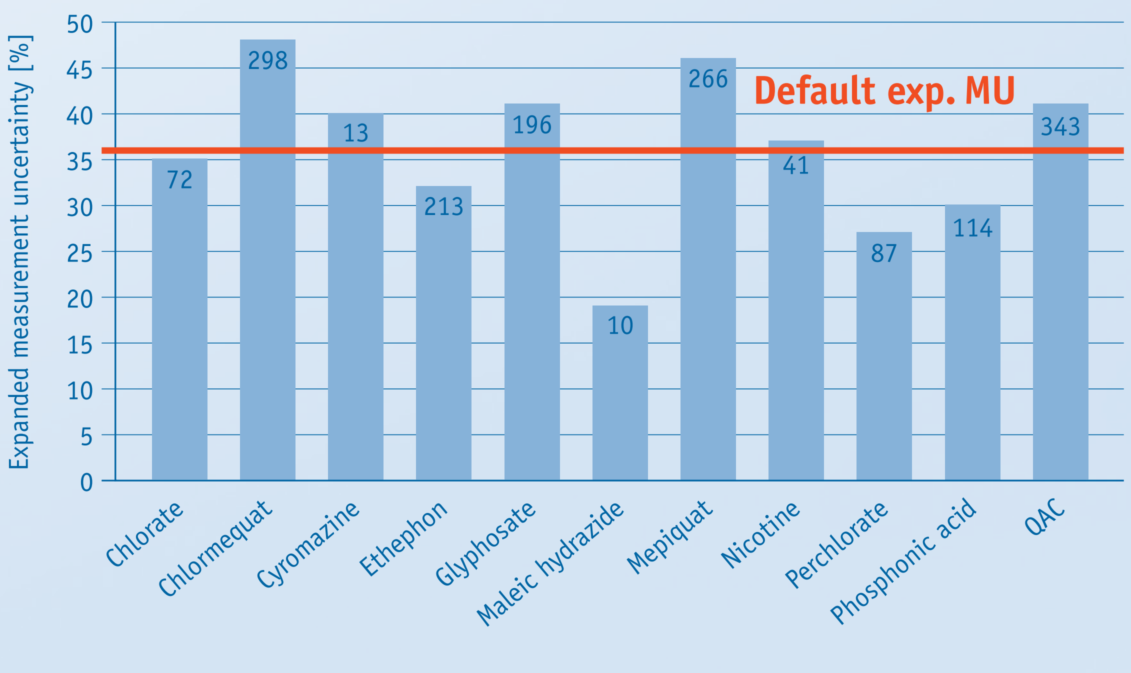
Finally, an overall mean value is calculated of the mean exp. MUs of all parameters. That overall mean is considered as the default exp. MU for single- and group-specific methods.

Results

The proficiency tests cover a broad concentration range (12 – 5000 µg/kg) and a high number of different matrices.

Based on >1600 data points and 26 different matrices a default expanded measurement uncertainty of 36 % is derived for single- and group-specific analytical methods.

A summary of the selected proficiency tests, the matrices and the expanded measurement uncertainties is provided in the table and the graph. The numbers above the bars in the graph indicate the number of data points, which were considered for the respective parameter.



Analyte	Matrix	Organiser	Test No.	No. of data points	Assigned value(s) [µg/kg]	Robust RSD [%]	Exp. MU [%]	Mean exp. MU [%]
Chlorate	Salad	Bipea	05-0419	8	169	22	**45**	**35**
	Basil	PROOF-ACS	P1410-RT	15	245	20	**41**	
	Courgette	PROOF-ACS	P1410-RT	15	57	13	**26**	
	Pear	PROOF-ACS	P1501-MRT	18	87	16	**33**	
	Tomato	PROOF-ACS	P1519-RT	16	28	14	**28**	
Chlormequat	Corn	Bipea	04-2219	8	53	32	**64**	**48**
	Corn	Bipea	05-2219	10	121	30	**60**	
	Corn	Bipea	06-2219	10	15	33	**67**	
	Corn	Bipea	07-2219	22	98	24	**49**	
	Flour	Bipea	05-0119	8	59	25	**51**	
	Corn flour	EUPT	SRM10 (2015)	75	167	18	**36**	
	Corn flakes	FAPAS	0978	26	342	14	**29**	
	Oat	FAPAS	0984	37	107	24	**48**	
	Oat	FAPAS	0990	41	282	21	**43**	
	Oat	FAPAS	0996	43	281	23	**46**	
	Pear	PROOF-ACS	P1501-MRT	18	45	19	**37**	
Cyromazine	Potato	PROOF-ACS	P1501-MRT	13	69	20	**40**	**40**
Ethephon	Salad	Bipea	05-0419	14	68	18	**35**	**32**
	Corn flour	EUPT	SRM10 (2015)	61	162	31	**62**	
	Grapes	FAPAS	19164	39	766	11	**22**	
	Grapes	FAPAS	19186	30	629	14	**28**	
	Pinapple	PROOF-ACS	P1305-RT	12	1018	7	**13**	
	Sweet pepper	PROOF-ACS	P1305-RT	10	19	14	**29**	
	Grapes	PROOF-ACS	P1305-RT	13	376	16	**32**	
	Pear	PROOF-ACS	P1501-MRT	17	170	17	**33**	
	Tomato	PROOF-ACS	P1519-RT	17	768	17	**34**	
Glyphosate	Corn	Bipea	06-2219	8	68	19	**38**	**41**
	Corn flour	EUPT	SRM10 (2015)	64	568	23	**46**	
	Oat	FAPAS	0984	21	453	11	**23**	
	Oat	FAPAS	0990	30	954	11	**23**	
	Oat	FAPAS	0996	30	523	22	**43**	
	Flax seeds	PROOF-ACS	P1304-RT	9	134	34	**69**	
	Black tea	PROOF-ACS	P1602-RT	10	86	19	**38**	
	Wheat flour	PROOF-ACS	Closed scheme	12	29	26	**51**	
	Wheat flour	PROOF-ACS	Closed scheme	12	44	17	**34**	
Maleic hydrazide	Potato	PROOF-ACS	P1501-MRT	10	5000	10	**19**	**19**
Mepiquat	Corn	Bipea	04-2219	8	35	23	**46**	**46**
	Corn	Bipea	05-2219	10	42	21	**43**	
	Corn	Bipea	06-2219	8	13	38	**77**	
	Corn	Bipea	07-2219	17	33	24	**48**	
	Flour	Bipea	05-0119	11	106	25	**51**	
	Corn flour	EUPT	SRM10 (2015)	76	114	19	**37**	
	Oat	FAPAS	0984	34	85	24	**47**	
	Oat	FAPAS	0990	41	145	20	**41**	
	Oat	FAPAS	0996	43	86	21	**41**	
	Pear	PROOF-ACS	P1501-MRT	18	38	16	**33**	
Nicotine	Mushrooms	PROOF-ACS	P1301-MRT	14	31	17	**33**	**37**
	Mushrooms	PROOF-ACS	P1301-MRT	14	567	15	**31**	
	Black tea	PROOF-ACS	P1602-RT	13	310	24	**48**	
Perchlorate	Tomato	PROOF-ACS	P1303-RT	12	427	7	**13**	**27**
	Water melon	PROOF-ACS	P1303-RT	12	31	13	**27**	
	Basil	PROOF-ACS	P1410-RT	18	483	14	**28**	
	Courgette	PROOF-ACS	P1410-RT	18	66	14	**27**	
	Tomato	PROOF-ACS	P1519-RT	18	172	18	**37**	
	Raspberries	PROOF-ACS	Closed scheme	9	39	14	**27**	
Phosphonic acid	Corn flour	EUPT	SRM10 (2015)	25	584	27	**55**	**30**
	Kaki	PROOF-ACS	P1411-RT	15	2471	7	**14**	
	Cucumber	PROOF-ACS	P1411-RT	14	198	22	**45**	
	Potato	PROOF-ACS	P1501-MRT	11	426	11	**21**	
	Pear	PROOF-ACS	P1501-MRT	15	1141	9	**18**	
	Tomato	PROOF-ACS	P1519-RT	16	311	18	**36**	
	Lemon	PROOF-ACS	Closed scheme	18	228	11	**21**	
Quaternary Ammonium Compounds: BAC C-12, BAC C-14	Egg	EUPT	A09	56	211/61	27	**53**	**41**
BAC C-12, DDAC	Salad	FAPAS	19177	67	273/417	22	**44**	
	Salad	FAPAS	19196	55	306/258	18	**37**	
BAC C-12, BAC C-14, BAC C16, DDAC C-10	Cream cheese	PROOF-ACS	P1306-RT	39	93/218/22/25	24	**48**	
	Salad	PROOF-ACS	P1306-RT	46	125/41/12/548	24	**47**	
	Carrot	PROOF-ACS	P1505-RT	32	23/17/39/54	12	**23**	
	Ice cream	PROOF-ACS	P1505-RT	48	79/62/20/169	16	**32**	
Overall (default) expanded measurement uncertainty for single- and group specific methods [%]								**36**

Discussion

The derived exp. MU of 36 % for SRM is lower than the default exp. MU for multi-residue methods (50 %). This is not surprising, since single- and group specific methods are best-fit approaches for a single parameter or a homogeneous group of parameters.

The default exp. MU of SRM is valid for various types of matrices. In contrast, the exp. MU for multi-residue methods is, strictly speaking, valid for fruit and vegetable matrices only.

The presented evaluation may still underestimate the state-of-the-art exp. MU, which is feasible for SRM. Some of the proficiency tests were the first proficiency tests ever of the respective parameters, and were performed shortly after the analytical methods were established in the labs (e.g. P1303-RT (perchlorate), P1410-RT (chlorate), P1411-RT (phosphonic acid)).

The evaluation confirms that the MUs do not only depend on the concentration of the analyte (Horwitz approach [3]) but also on the analytical approach (single or multi-residue approach) and on the type of matrix analysed.

However, the default exp. MU of SRM might not be valid for all types of SRM. For challenging analytes like dithianon or dithiocarbamates an exp. MU of 36 % is certainly not feasible. For less challenging analytes like nitrate in vegetables even lower exp. MU of about 20 % are achievable.

Conclusion

An exp. MU of 36 % is feasible for the quantification of pesticides and contaminants by single- and group specific methods in food. If applied for the evaluation of proficiency tests an expanded measurement uncertainty of 50 % underestimates the state-of-the-art in single- and group-specific methods. The results of the presented evaluation should be taken into consideration for the definition of evaluation criteria in proficiency tests for single- and group specific methods.

Acknowledgement

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REFERENCES: Proficiency tests: Bipea No. 05-0119, 04-2219, 05-2219, 06-2219, 07-2219, 05-0419; EUPT No. EUPT-SRM10 (2015), EUPT-A09 (2014); FAPAS No. 19164, 19177, 19186, 19196, 0978, 0984, 0990, 0996; PROOF-ACS No. P1301-MRT, P1303-RT, P1306-RT, P1410-RT, P1411-RT, P1501-MRT, P1505-RT, P1519-RT, P1602-RT, 3 closed schemes. ■ **[1]** European Commission and Directorate General for Health and Food Safety, "SANTE/11945/2015 Guidance document on analytical quality control and method validation procedures for pesticide residue analysis in food and feed," 2015. ■ **[2]** NIST, "Uncertainty of Measurement Results - Expanded uncertainty and coverage factor," The NIST Reference on Constants, Units, and Uncertainty. [Online]. Available: http://physics.nist.gov/cuu/Uncertainty/coverage.html. [Accessed: 21-Apr-2016]. ■ **[3]** W. Horwitz, "Evaluation of Analytical Methods Used for Regulation of Foods and Drugs," Anal. Chem., vol. 54, no. 1, p. 67A–76A, 1982.