

SPECTROMETRIC DETERMINATIONS OF SELECTED HERBICIDES IN MODELLED AQUEOUS SOLUTIONS

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ABSTRACT

The adsorption spectra of three herbicides, namely MCPA, glyphosate and metribuzin have been measured in aqueous solution using ATR-FTIR spectroscopic and UV-VIS spectrophotometric methods in order to establish calibration curves for future sorption and AOP remediation experiments. Our experimental data are discussed and compared with similar molecules, when such data were available in the literature.

KEY WORDS

UV-VIS spectrophotometry, ATR-FTIR spectroscopy, glyphosate, MCPA, metribuzin

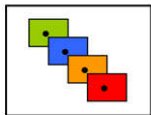
Introduction

A pesticide is any chemical substance used to kill, repel, or control certain forms of plant or animal life that are considered to be pests. Pesticides include *herbicides* for destroying weeds and other unwanted vegetation; *insecticides* for controlling a wide variety of insects; *fungicides* used to prevent the growth of molds and mildew; *disinfectants* for preventing the spread of bacteria; and *rodenticides* used to control mice and rats, etc.

Herbicides can be separated into organic or inorganic materials. *Organic herbicides* have a carbon based molecular structure and usually act by altering the normal growth pattern of the plant. Organic herbicides may be further divided into two major groups - the petroleum oils and the synthetic organic herbicides. The petroleum oils, refined from crude oil, can be used as either herbicides or insecticides. When formulated as herbicides, they are usually applied without dilution. Synthetic organic herbicides are artificially created in laboratories, and they are made up of carbon, hydrogen, often nitrogen, and as well as other elements. Included among the common synthetic organic herbicides are 2,4-D, and glyphosate. *Inorganic herbicides* are often in the form of a salt, or contain a metal that is toxic to plants, often preventing proper uptake of water or inhibiting movement of material across cell walls. Inorganic herbicides are chemical compounds which do not have a carbon structure. The inorganics include such common materials as salt, copper sulfate, sulfuric acid, and sodium chlorate. These herbicides are extremely persistent and have caused serious soil pollution problems in some areas. Many are restricted materials (Eldridge 2008).

Devising a simple classification scheme for herbicides based on their chemical group is difficult. To classify herbicides by chemical group requires at least 20 different categories, only a few of which will be mentioned here (Eldridge 2008):

- *Phenoxy herbicides* are used in both crop and non-crop areas for control of most annual and perennial broadleaf weeds. Some commonly used phenoxyes include 2,4-D, MCPA, dichlorprop, and 2,4-DB. These herbicides are primarily plant growth regulators and affect the actively growing tissue of the plant. The ester formulations of the phenoxyes are relatively volatile and turn into a gas during hot summer days. Care should be taken not to use them around susceptible broadleaf crops and ornamentals.
- *Triazines* are used to control annual grasses and broadleaf weeds. Some commonly used triazines include atrazine, simazine, and metribuzin. The triazines are primarily used as non-selective pre-emergent herbicides. Triazines affect plants by inhibiting their ability to photosynthesize.
- *Thiocarbamates* are used for control of annual grass seedlings and broadleaf weed seedlings. EPTC is a commonly used thiocarbamate. They inhibit the meristematic growth of plants, such as root and shoot tips and are applied as a pre-plant, soil incorporated treatment.
- *Ureas and uracils* have several similar uses and their modes of action have many features in common. Diuron and tebuthiuron are commonly used ureas, and bromacil is a widely used uracil. These compounds are primarily applied to soil as pre-emergence herbicides, but they also provide post-emergence control for certain plants. The ureas and uracils affect plants by inhibiting their ability to photosynthesize.
- *Benzoic acid herbicides* are used in both crop and non-crop areas for control of numerous broadleaf weeds and annual grasses. Banvel is a commonly used member of this group. The benzoics are effective when applied either



to the plant foliage or to the soil and work as plant growth regulators that affect the actively growing tissues of plants.

- *The acetanilide herbicides* are used for control of many annual grasses and broadleaf weeds. Common acetanilides include alachlor, acetochlor, metolachlor, and pronamide. This group can be applied either pre-emergence or pre-planting in crop areas.
- *Sulfonylureas* - one of the most recently developed groups of herbicides, the sulfonylureas are highly active compounds used at extremely low rates. They are used to control many broadleaf plants in small grain crops, pastures, and noncrop areas. Commonly used sulfonylureas include chlorsulfuron, triasulfuron, sulfometuron, and metsulfuron. These compounds are usually applied as foliar treatments; however, they also control newly emerging broadleaf seedlings. Chlorsulfuron and sulfometuron are sulfonylureas that are more persistent in nature and will carry over into a second year when applied in high-pH soils. Extremely low residues from wind drift or in wind-blown soil can cause significant losses in certain crops including corn, potatoes, and sugar beets.
- *Imidazolinones* includes imazethapyr, imazamethabenz, and imazapyr. This group act as biosynthesis inhibitors within the actively growing plant. These are broad spectrum herbicides and may be used against grass, broadleaf annuals, biennials, and perennials, vines, brush, and trees. Care must be taken around trees as root uptake from soil may result in death.

Herbicides are applied in a variety of ways, and the way that they are used affects environment differently. Analysis of herbicides has mainly been accomplished by gas chromatography (e.g. Arkan et al. 2016), liquid chromatography (e.g. Papadakis and Mourkidou 2002; Khrolenko and Wieczorek 2005, Ramirez et al. 2014), ion chromatography (e.g. Zelenkova and Vinokurova 2008, He et al. 2014), micellar electrokinetic chromatography (e.g. Huertas-Perez et al 2006), capillary zone electrophoresis (e.g. Molina et al. 2007) or capillary electrophoresis (e.g. Corbera et al 2005). All these methods are expensive, require long separation times and sometimes need the development of extremely complex gradient for the separation. For rapid and cheap determination of these herbicides are therefore useful in different spectrometric and spectrophotometric methods.

Materials and methods

All of the experiments were performed with p.a. chemicals and water solutions of pesticides prepared from commercial herbicide products. Construction the analytical calibration curves using commercial products is appropriate e.g. to determine removal efficiency of pesticides by various AOP methods. On the other hand, use of pure chemicals (p.a.) is suitable e.g. for monitoring of these substances in environment.

- ATR-FTIR Spectrophotometric determinations were realized on Infrared Fourier Transform Spectroscopy with ATR technique - Attenuated Total Reflectance (Varian 660 Dual MidIR MCT/ TGS Bundle). Samples were directly applied to a diamante crystal of ATR and resulting spectra of them were corrected for background air absorbance. The spectra were recorded using a Varian Resolutions Pro and were measured in the region 4000 – 400 cm^{-1} ; each spectrum was measured 36 times, at resolution 4. To minimize differences between spectra due to baseline shifts, the spectra were baseline corrected and ATR-corrected.
- UV-VIS Spectrophotometric determinations were realized on Spectrophotometer TermoSpectronic GENESISTM in 1 cm quartz cuvette. The construction of calibration curves was realized by methods is reported in following session. All of measurements were realized in triplicates.

Glyphosate determination with carbon disulphide and copper solution

Due to the absence of chromophore or fluorophore groups in the structure of glyphosate, the direct spectrophotometric and fluorometric method for determination of glyphosate has not been described. The present method is based on reaction of glyphosate with carbon disulphide to convert the amine group into dithiocarbamic acid which was further followed for complex formation with copper in the presence of ammonia (Fig. 1., 2.). The absorbance of the resulting yellow coloured copper dithiocarbamate complex was measured at 435 nm (Rasul Jan et al 2009).

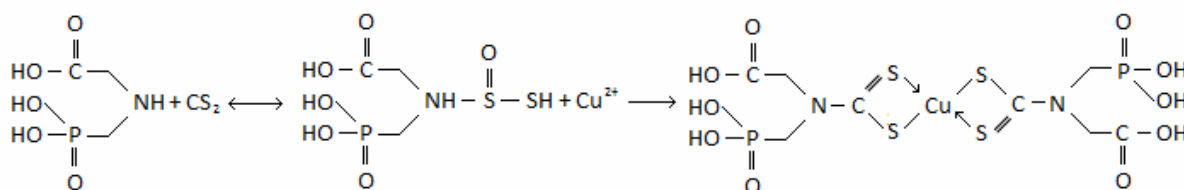
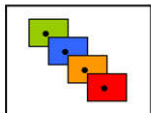


Fig. 1. Proposed reaction mechanism for spectrophotometric determination of glyphosate.



Reagents:

- *ammonical copper nitrate solution* (1 mg/L): 0.1288 g of copper nitrate dihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$) was dissolved in 20 mL distilled water and diluted with concentrate ammonia solution to 100 mL in volumetric flask.
- *carbon disulphide solution* (1%): was prepared by mixing 2 mL CS_2 in ethanol and diluted to 200 mL with ethanol.
- *glyphosate stock solution* (10.8 g/L) was prepared by dissolving 2.8 mL of FONDO herbicide in distilled water and diluted with distilled water up to 100 mL in volumetric flask.
- *working solutions*: prepared by dilution of the stock solution with distilled water (Tab. 1.)

Tab. 1. Volumes of stock solution and water for working solutions preparing

Concentration C (mg/L)	10,08	20,16	30,24	40,32	50,40	60,48	70,56	80,64	90,72	100,08
Stock solution V_1 (mL)	10	20	30	40	50	60	70	80	90	100
Volumetric flask V_2 (mL)	100	100	100	100	100	100	100	100	100	100

Procedure:

- to 4 mL of sample (solutions in concentration range) was added 2,5 mL of carbon disulphide solution, immediately 1 mL of copper solution and adjusted the volume to 50 mL with distilled water,
- after 30 minutes the stain remains and the absorbance is measured at 435 nm against a blank prepared in the same way.

For the decreasing of detection limits this procedure can be upgraded with next steps containing chloroform extraction (was not realized): The solutions after mixed agent addition were transferred to separatory funnels, 10 mL of chloroform was added and shaken well for 2 min. The two phases were allowed to separate. The chloroform layer was removed and the absorbance of yellow coloured complex extracted was measured at 435 nm against reagent blank.

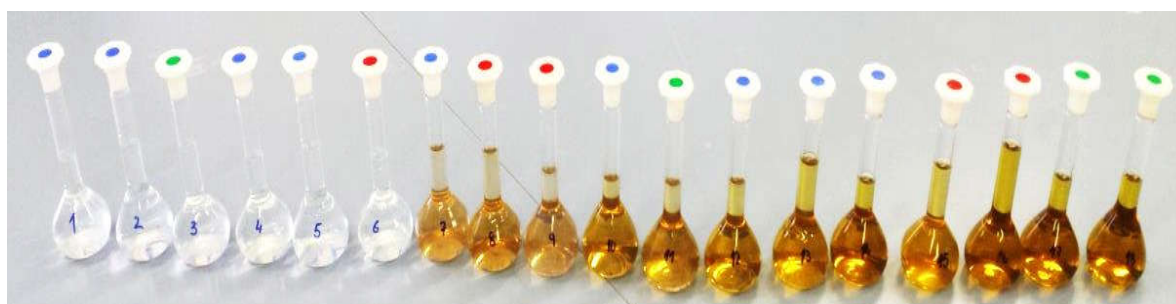


Fig.2. Characteristic yellow coloured complex for glyphosate UV-VIS measurement (working solutions)

Metribuzin determination with copper solution

Metribuzin reacted with copper to give a stable complex in the presence of ammonia (0.2 mol/L) at pH 10.5 (Fig. 3.). The resulting yellow coloured complex has absorption maxima at 340 nm. (Sash et al. 2009)

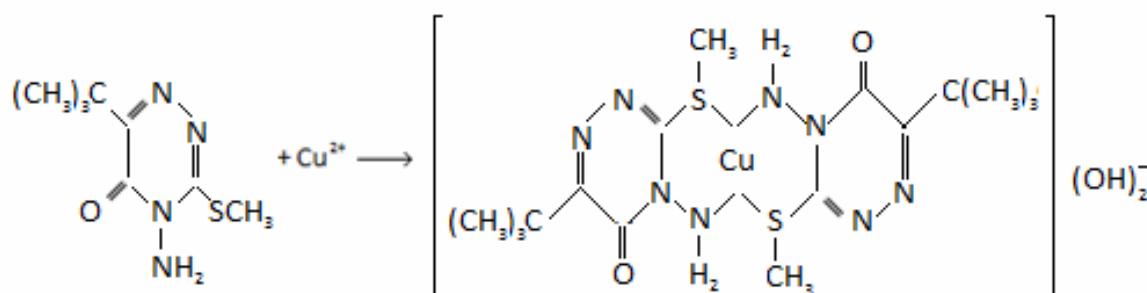
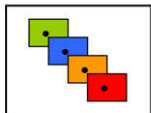


Fig. 3. Proposed reaction mechanism for spectrophotometric determination of metribuzin.



Reagents:

- *ammonical copper nitrate solution* (1 mg/L): 0.1975 g of copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was dissolved in 10 mL distilled water, added 1.4 mL of concentrated ammonia solution and diluted to 100 mL in volumetric flask.
- *metribuzin stock solution* (1000 mg/L) was prepared by dissolving 0.7145 g of SENCO 3 herbicide in distilled water (5 min. of sonification is needed) and diluted with distilled water up to 500 mL in volumetric flask.
- *working solutions*: were prepared by dilution of the stock solution with distilled water (Tab. 2.).

Tab. 2. Volumes of stock solution and water for working solutions preparing

Concentration C (mg/L)	100,0	200,0	300,0	400,0	500,0	600,0	700,0	800,0	900,0	1000,0
Stock solution V_1 (mL)	10	20	30	40	50	60	70	80	90	100
Volumetric flask V_2 (mL)	100	100	100	100	100	100	100	100	100	100

Procedure:

- to 4 mL of sample (solutions in concentration range) was added 1 mL of mixed reagent and adjusted the volume to 25 mL with distilled water,
- after 30 minutes the stain remains and the absorbance is measured at 340 nm against a blank prepared in the same way.

For the decreasing of detection limits this procedure can be upgraded with next steps containing chloroform extraction (was not realized). The solutions after mixed agent addition were transferred to separatory funnels, 10 mL of chloroform was added and shaken well for 2 min. The two phases were allowed to separate. The chloroform layer was removed and the absorbance of yellow coloured complex extracted was measured at 340 nm against reagent blank.

MCPA determination at 278 nm

The absorption spectra for MCPA solution were recorded in wavelength ranging from 190 – 350 nm. Concentration changes of MCPA were determined by monitoring the absorption peak at a maximum wavelength of 278 nm.

Reagents:

- *MCPA stock solution* (500 mg/L) was concentration of commercial preparation AMINEX 500 SL.
- *working solutions*: were prepared by dilution of the stock solution with distilled water (Tab. 3.).

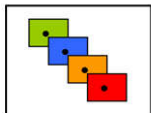
Tab. 3. Volumes of stock solution and water for working solutions preparing

Concentration C (mg/L)	50,0	100,0	200,0	300,0	400,0	500,0
Stock solution V_1 (mL)	10	20	40	60	80	100
Volumetric flask V_2 (mL)	100	100	100	100	100	100

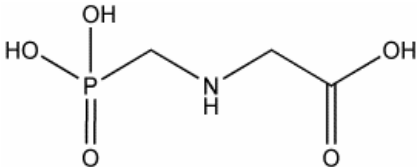
Results and discussion

Glyphosate

Glyphosate, chemically [N-(phosphonomethyl) glycine] is a post-emergence nonselective herbicide, used for the control of a wide variety of weeds. Due to its relatively low toxicity to mammals; it has become the most widely used herbicide. With nearly 650 000 tons annually widespread, glyphosate is the best-selling pesticide in the world. It is also the top ranked herbicide in the European Union, as it has been used in 40 % of agricultural land (Zhang et al. 2011). According to the "List of authorized plant protection products and plant protection products authorized for parallel trade" are to 31/10/2015 the Slovak Republic authorized for example following products containing glyphosate: COSMIC (361 g/L), FONDO (360 g/L), FOZAT 480 (360 g/L), JETSTAR (360 g/L), KAPAZIN (360 g/L), KAPUT (360 g/L), ROUNDUP AKTIV (170 g/L), ROUNDUP BIAKTIV (360 g/L), ROUNDUP EXPRES 6H (7.2 g/L) or TOUCHDOWN SYSTEM 4 (360 g/L).



Tab. 4. Physicochemical properties of glyphosate (PAN Pesticides Database 2015)

	CAS Number:	1071-83-6
	Molecular Weight (g/mol)	169.1
	Water Solubility (mg/L)	11600
	Adsorption Coefficient (K_{oc})	6920
	Hydrolysis Half-life (Days)	35.0
	Aerobic Soil Half-life (Days)	96.0
	Anaerobic Soil Half-life (Days)	22.0

The glyphosate IR spectra is shown at Fig. 4. at wavenumber from 400 – 2000 cm^{-1} .

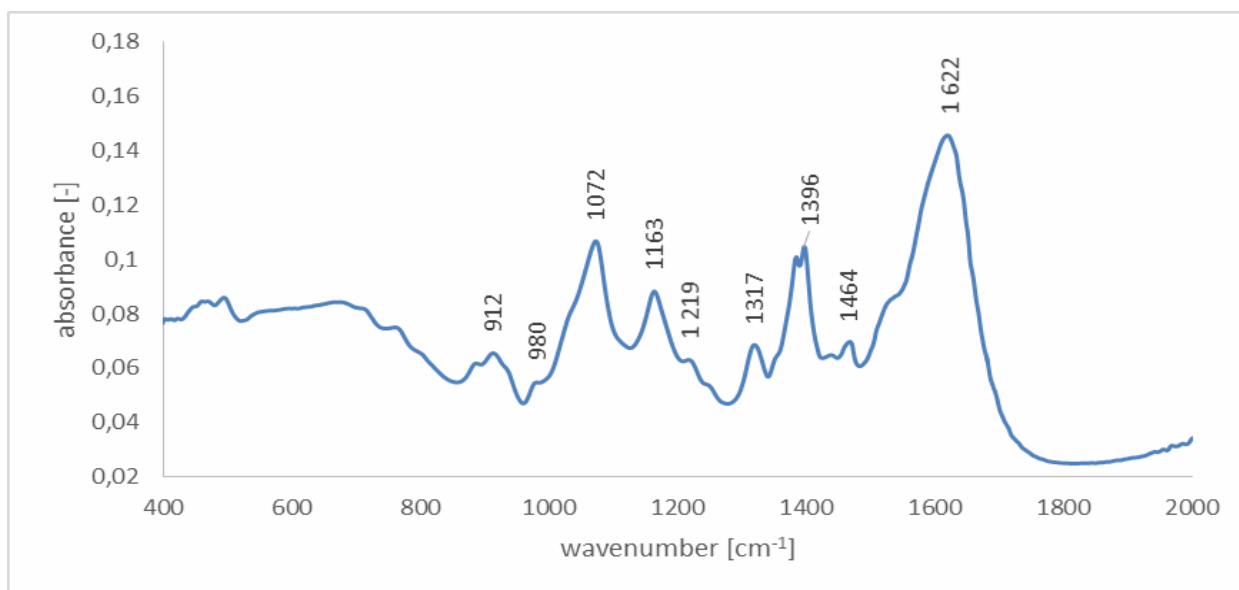


Fig. 4. Infrared spectrum of glyphosate

Glyphosate IR absorption bands appear at 1396, 1317, 1163, 1072 (shoulder) and 980 cm^{-1} , and correspond to the $\nu_s(\text{C-O})$, $\nu(\text{C-O-P})$, $\nu_a(\text{P-OH})$ (antisymmetric and symmetric) vibration modes, respectively. According to Sheals et al. (2009) these bands reflect the formation of monodentate mononuclear innersphere complexes (Waiman et al. 2013). Wavenumber at 1464 cm^{-1} refers to $\nu(\text{C-OH})$ bond. Band at 1219 cm^{-1} is attributed to $\nu(\text{P-OH})$.

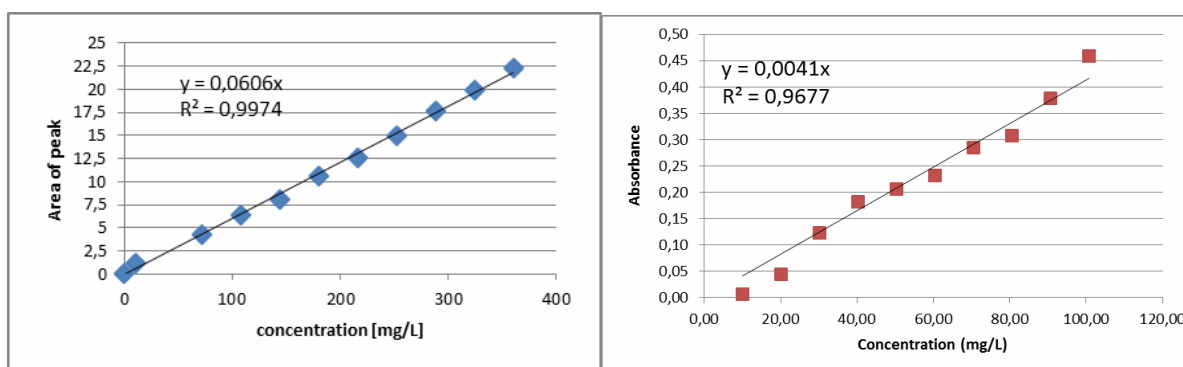
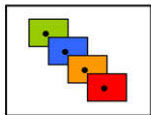


Fig. 5. Calibration curves for ATR-FTIR spectroscopy a UV-VIS spectroscopy of glyphosate.

Calibration curve for FTIR-ATR (Fig. 5.) was constructed as dependence concentration of solution (10 – 360 mg/L) to area of peak (1040 – 1690 cm^{-1}) in the form:

$$A = 0.00606 \times c \quad R^2 = 0.9974$$

Calibration curve for UV-VIS (Fig. 5.) range was reported as linear between 10 – 100 mg/L (A = 0 – 0.459) in the form:



$$A = 0.0041 \times c \quad R^2 = 0.9677$$

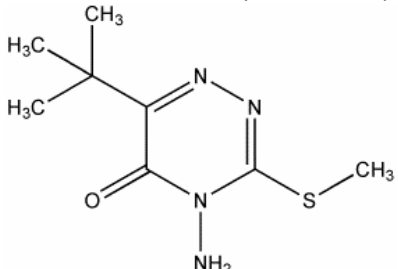
where A is absorbance and c is concentration of glyphosate in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{4}{n} \times \frac{A}{0.0041}$$

Metribuzin

Metribuzin, chemically 4-amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5-one is an herbicide used both pre- and post-emergence in crops. It acts by inhibiting photosynthesis by disrupting photosystem. According to the "List of authorized plant protection products and plant protection products authorized for parallel trade" are to 31/10/2015 the Slovak Republic authorized for example following products containing metribuzin: SENCOR 70 WG (700 g/kg), SENCOR LIQUID (600 g/kg).

Tab. 5. Physicochemical properties of metribuzin (PAN Pesticides Database 2015)

	CAS Number: 21087-64-9
	Molecular Weight (g/mol) 214.3
	Water Solubility (mg/L) 1030
	Adsorption Coefficient (K_{oc}) 106.0
	Hydrolysis Half-life (Days) 4760
	Aerobic Soil Half-life (Days) 140.0
	Anaerobic Soil Half-life (Days) 276.0

The metribuzin IR spectra is shown at Fig. 6. at wavenumber from 400 – 4000 cm^{-1} . In the spectrum, the region of CO_2 from the atmosphere is not presented.

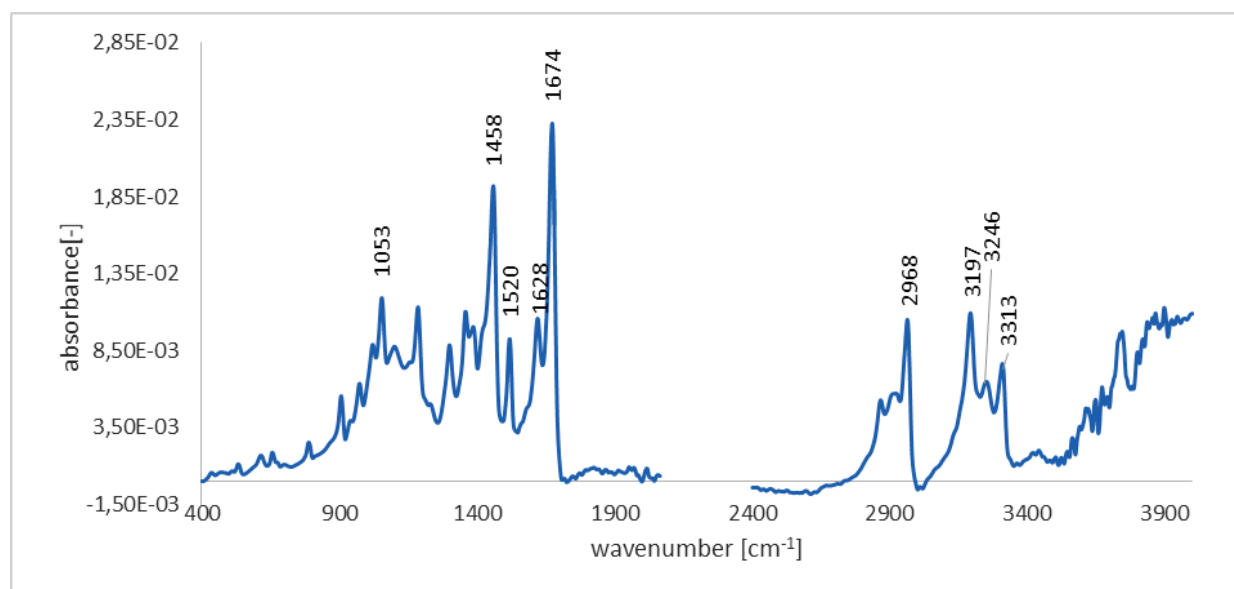


Fig. 6. Infrared spectrum of metribuzin

In the spectra of adsorbed metribuzin, the band at 1674 cm^{-1} that corresponded to the carbonyl (amide) of the herbicide appeared as well as a small shoulder assigned to the NH_2 deformation band at 1617 cm^{-1} (Undabeytia 2010). The band at 1053 cm^{-1} is diagnostic of the thioether group $-\text{S}-\text{CH}_3$. The $-\text{NH}_2$ group shows both symmetric and asymmetric stretching vibrations at 3197 and 3313 cm^{-1} . The C–N absorption is found near 1520 cm^{-1} (Maqueda et al. 2009).

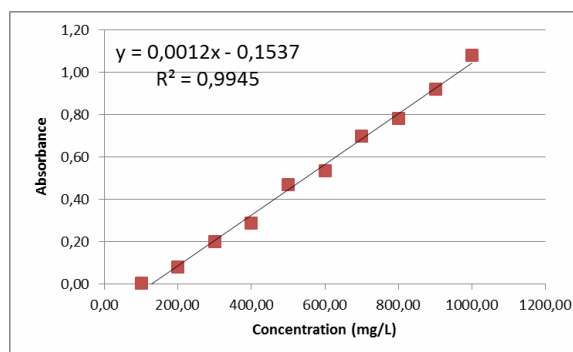
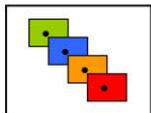


Fig. 7. Calibration curves for a UV-VIS spectroscopy of metribuzin.

Calibration curve for UV-VIS (Fig. 7.) range was reported as linear between 100 – 1000 mg/L ($A = 0 - 1.080$) in the form:

$$A = 0.0012 - 0.1537 \times c \quad R^2 = 0.9945$$

where A is absorbance and c is concentration of metribuzin in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{4}{n} \times \frac{(A + 0.1537)}{0.0012}$$

MCPA

MCPA, chemically 2-methyl-4-chlorophenoxyacetic acid is used to control a wide range of broadleaf weeds. It accumulates in the meristematic tissue of plants, where growth occurs there, it stimulates plant hormones, causing uncoordinated plant growth that disrupts both new seedlings and existing plants. According to the “List of authorized plant protection products and plant protection products authorized for parallel trade” are to 31/10/2015 the Slovak Republic authorized for example following products containing MCPA: DICOPUR M 750 (750 g/l), AMINEX 500 SL (500 g/l).

Tab. 6. Physicochemical properties of MCPA (PAN Pesticides Database 2015)

	CAS Number:	94-74-6
	Molecular Weight (g/mol)	200.6
	Water Solubility (mg/L)	29390
	Adsorption Coefficient (K_{oc})	74.0
	Aerobic Soil Half-life (Days)	15.0

The MCPA IR spectra is shown at Fig. 8. at range of wavenumber 500 – 3000 cm^{-1} .

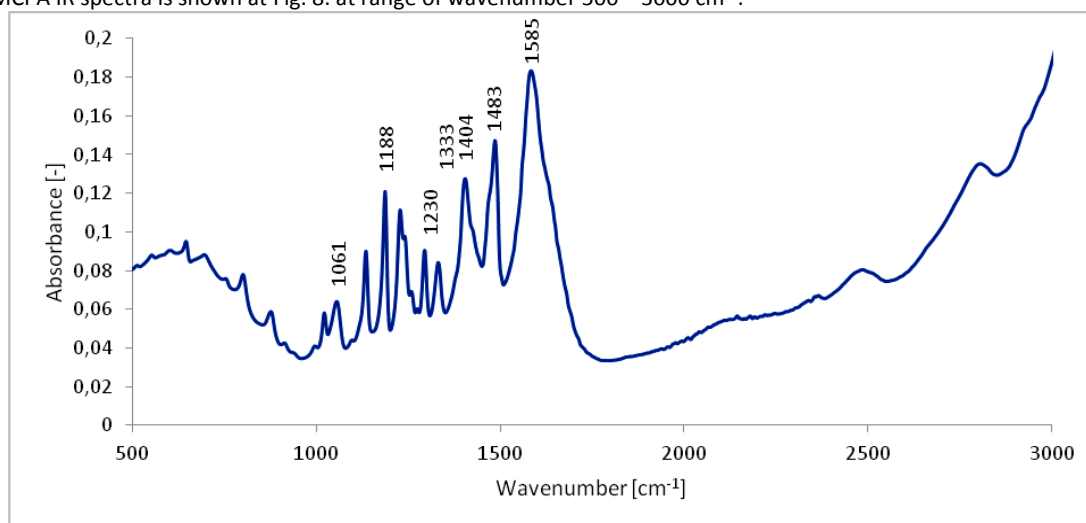
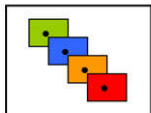


Fig. 8. Infrared spectrum of MCPA



Band observed at 1483 cm^{-1} is assigned as the scissoring mode of $-\text{CH}_2$. Bands of hydrocarbons due to CH_2 twisting and wagging vibrations are observed in the region $1182 - 1400\text{ cm}^{-1}$. The position of the $\nu(\text{C}-\text{O})$ stretch band is assigned for phenoxy group is at 1230 and 1333 cm^{-1} .

Calibration curve for FTIR-ATR (Fig. 9.) was constructed as dependence concentration of solution ($0 - 500\text{ mg/L}$) to area of peak ($1117 - 1510\text{ cm}^{-1}$) in the form:

$$A = 0.0155 \times c - 0.5914 \quad R^2 = 0.9842$$

Calibration curve for UV-VIS (Fig. 9.) range was reported as linear between $50 - 500\text{ mg/L}$ ($A = 0 - 0.607$) in the form:

$$A = 0.0008 + 0,2527 \times c \quad R^2 = 0.9429$$

where A is absorbance and c is concentration of MCPA in mg/L . For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{50}{n} \times \frac{(A - 0.2527)}{0.0008}$$

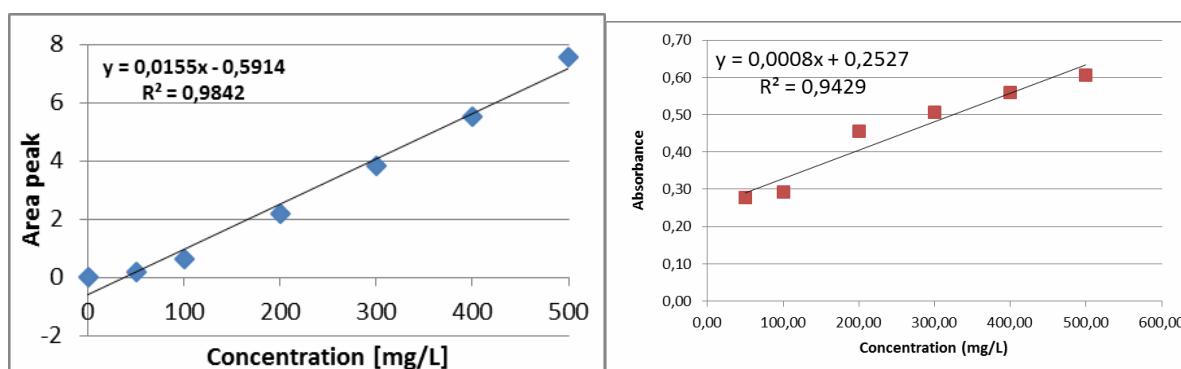


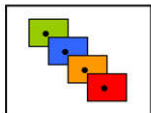
Fig. 9. Calibration curves for ATR-FTIR spectroscopy a UV-VIS spectroscopy of MCPA

Conclusion

Since their discovery in 1760s, pesticides have greatly contributed to improve the yield and quality of plants, and to ensure crop production. Today, modern agriculture is very dependent on pesticides, since 4.6 million tons of chemical pesticides are annually sprayed into the environment (Zhang et al. 2011). Today, MCPA, glyphosate, atrazine, and their main breakdown products, such as amino-methyl phosphoric acid (AMPA) and desethyl-atrazine (DEA), are responsible for an almost universal contamination of soil, sediment, surface water and groundwater. It is therefore, important to monitor their occurrence in the environment and study the removal technologies.

REFERENCES

- Arkan, T., Csámpai, A. and Molnár-Perl, I. 2016: Alkylsilyl derivatization of glyphosate and aminomethylphosphonic acid followed by gas chromatography mass spectrometry. *Microchem. J.*, 125, 219 - 223.
- Corbera, M., Hidalgo, M., Salvado, V. and Wiczorek, P. P. 2005: Determination of glyphosate and aminomethylphosphonic acid in natural water using the capillary electrophoresis combined with enrichment step. *Anal. Chim. Acta*, 540, 3 - 7.
- Eldridge, B. F. 2008: Pesticide application and safety training for applicators of public health pesticides. California Department of Public Health. -[on-line] Available on - URL: http://westnile.ca.gov/special/category_a/
- He, J., Yu, J. S., Hou, Y. J., Zhu, Z. Y., Huang, Z. P., Wang, M. H., Zhong, N. F., Zhu, Y. 2014: Determination of iminodiacetic acid in the glyphosate by ion chromatography. *Chinese Chemical Letters*, 25, 10, 1392 - 1394.
- Huertas-Perez, J. F., Iruela, M. O., Campana, A. M. G., Casado, A. G. and Navarro, A. S. 2006: Determination of herbicide metribuzin and its major conversion products in soil by micellar electrokinetic chromatography, *J. Chromatogr. A* 1102, 280 - 286.



- Jan, M. R., Shah, J. Muhammad, M. and Ara, B. 2009: Glyphosate herbicide residue determination in samples of environmental importance using spectrophotometric method. *Journal of Hazardous Materials*, 169, 742 – 745.
- Khrolenko, M. V. and Wiczorek, P. P. 2005: Determination of glyphosate and its metabolite aminomethylphosphonic acid in fruit juices using supported-liquid membrane preconcentration method with high-performance liquid chromatography and UV detection after derivatization with p-toluenesulphonyl chloride. *J. Chromatogr. A* 1093, 111 – 117.
- Maqueda, C., Partalm, P., Villaverde, J. and Perez-Rodriguez, J. L. 2009, Characterization of sepiolite-gel-based formulations for controlled release of pesticides. *Appl. Clay Sci.*, 46, 3, 289 – 295
- Molina, C. Q., Campana, A. M. G., Iruela, L. O. and Olmo, M. 2007: Large volume sample stacking in capillary zone electrophoresis for the monitoring of the degradation products of metribuzin in environmental samples, *J. Chromatogr. A* 1164, 320 – 328.
- PAN Pesticides Database – Chemicals. -[on-line] Available on - URL: <http://www.pesticideinfo.org/>
- Papadakis, E. N. and Mourkidou, E. P. 2002: Determination of metribuzin and major conversion products in soils by microwave-assisted water extraction followed by liquid chromatographic analysis of extracts. *J. Chromatogr. A* 962, 9 – 20.
- Ramirez, C. E., Bellmund, S. and Gardinali, P. R. 2014: A simple method for routine monitoring of glyphosate and its main metabolite in surface waters using lyophilization and LC-FLD + MS/MS. Case study: canals with influence on Biscayne National Park. *Sci. Tot. Environ*, 496, 389 - 401.
- Shah, J. Jan, M. R., Ara, B. and Mohammad, M. 2009: Spectrophotometric method for determination of metribuzin herbicide and application of factorial design in optimization of various factors. *J. Haz. Mat.*, 164, 918 – 922.
- Sheals, J., Sjöberg, S., Persson, P. 2002: Adsorption of glyphosate on goethite: molecular characterization of surface complexes. *Environ. Sci. Technol.*, 36, 3090 – 3095
- Undabeytia, T., Recio, E., Maqueda, C., Morillo, E., Gómez-Pantoja, E. and Sánchez-Verdejo T. 2010: Reduced metribuzin pollution with phosphatidylcholine-clay formulations. *Pest. Manag. Sci.* 67, 3, 271 – 278
- Waiman, C. V., Avena, M. J., Regazzoni, A. E. and Zanini, G. P. 2013: A real time in situ ATR-FTIR spectroscopic study of glyphosate desorption from goethite as induced by phosphate adsorption: effect of surface coverage. *J. Colloid Interface Sci.*, 394, 485 – 489
- Zelenkova, N. F. and Vinokurova, N. G. 2008: Determination of glyphosate and its biodegradation products by chromatographic methods. *J. Anal. Chem.* 63, 871 – 874.
- Zhang, W., Jiang, F. and Ou, J. 2011: Global pesticide consumption and pollution: with China as a focus. *Proc. Int. Acad. Ecol. Env. Sci.* 1, 125 – 144.

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