



IDENTIFICATION AND QUANTIFICATION OF HERBICIDE CONTAMINANTS FROM INPUTS USED FOR ORGANIC AGRICULTURE

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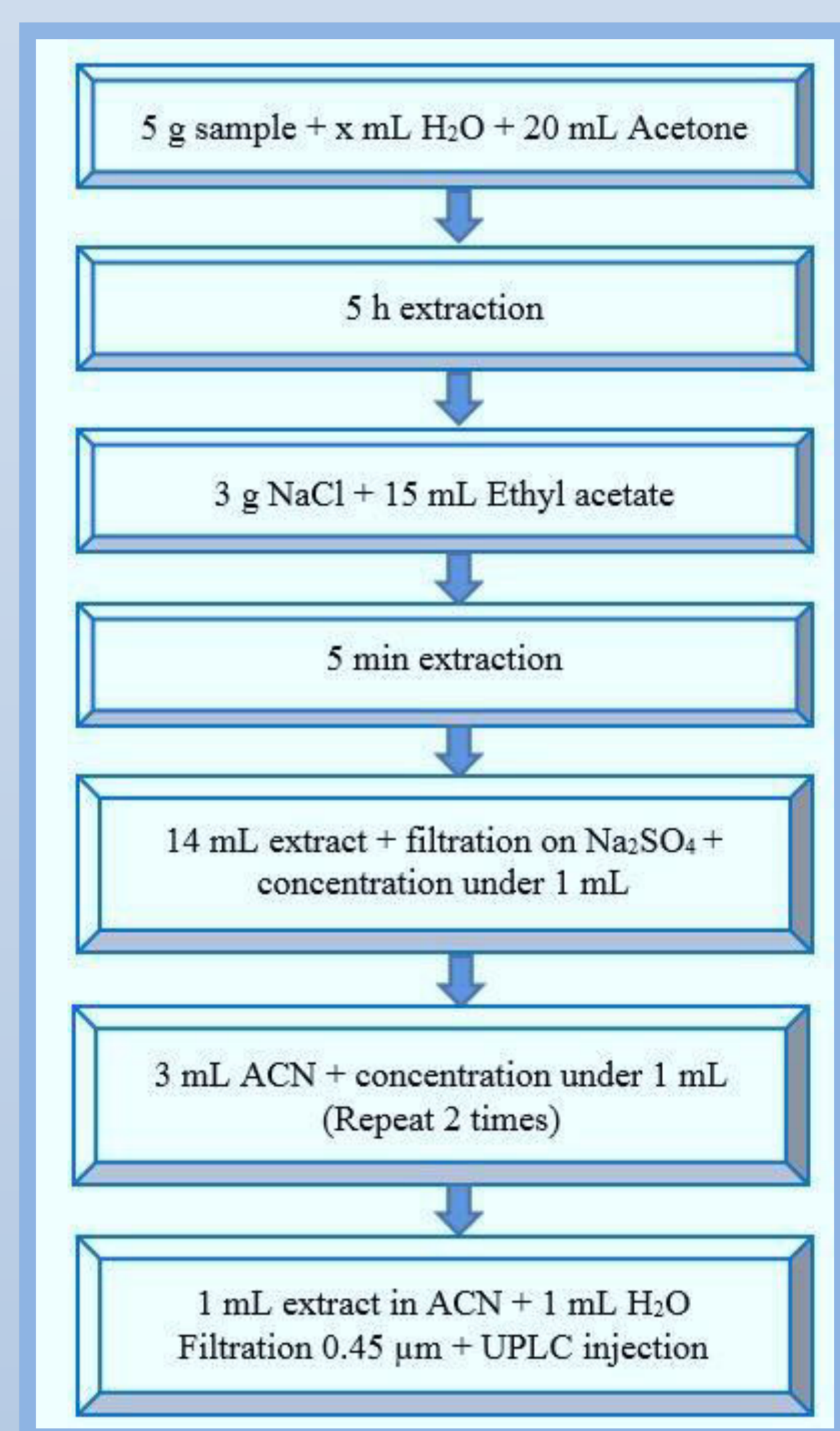
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INTRODUCTION

- » Organic agriculture is increasing in Romania, especially due to a better understanding of the effect of conventional agriculture on biodiversity.
- » There is a gap in the regulations regarding contaminants in organic inputs, there for they are no available standard methods used to determine contaminants such as pesticides form inputs (fertilisers) used for organic farming.
- » This study aims to develop and validate a quantification method to analyse the triazine contaminants (Hexazinone, Simazine, Simetryne, Atrazine, Ametryn, Propazine, Terbutylazine, Prometryn) from lignosulfonate fertilizers using UPLC-PDA.

MATERIALS AND METHODS



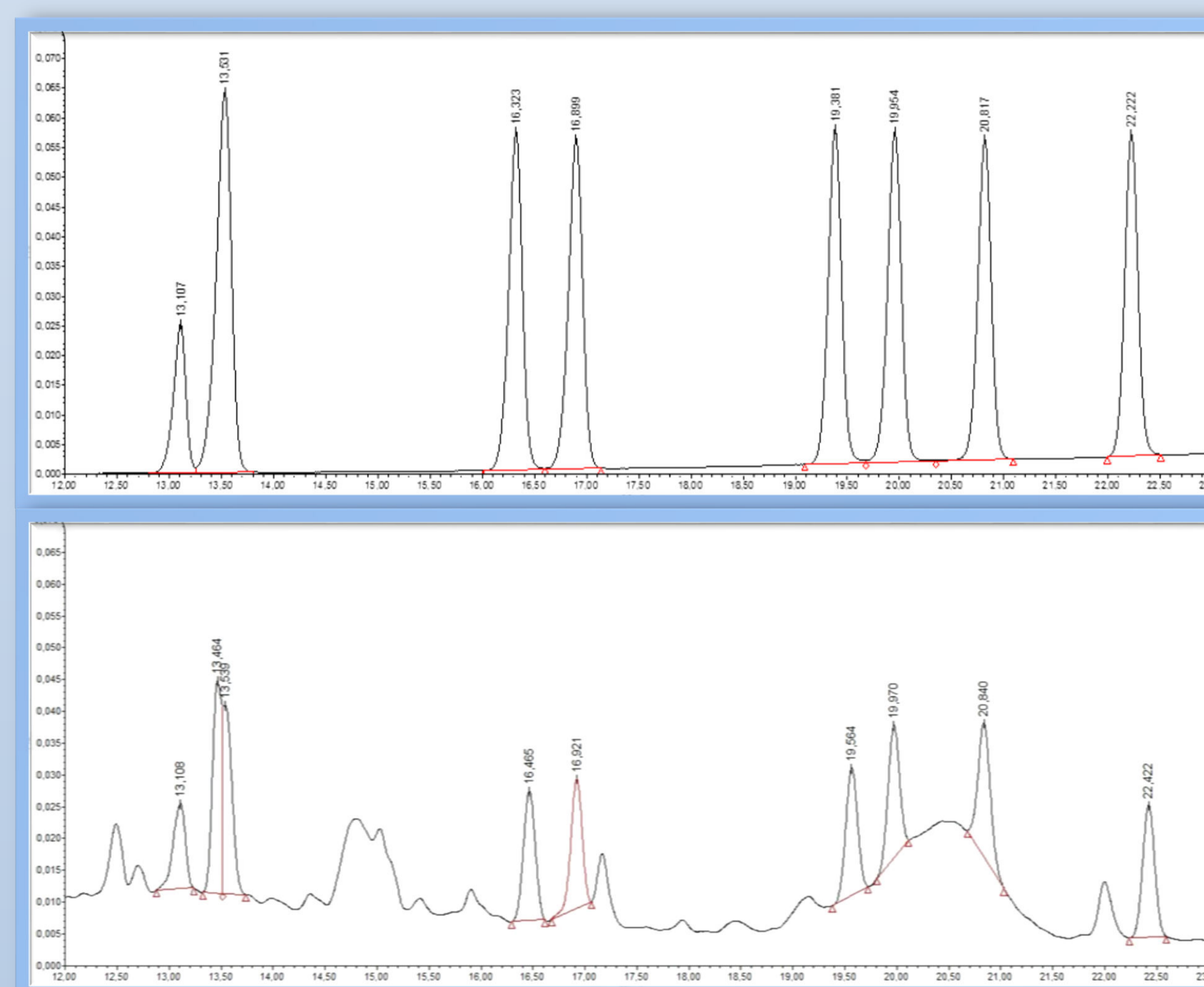
Schematic representation of the extraction and concentration of fertilizer samples

- Waters Acquity I chromatographic system equipped with a binary pump, autosampler, PDA detector and a Zorbax Eclipse Plus C18 4.6 x 100 mm, 5 µm column;
- Samples were maintained at 10 ° C, the injection volume was 10 µL;
- Column was kept at 30 ° C;
- PDA detector was set to register the spectrum from 210 to 320 nm, wavelength of 245 nm for Hexazinone herbicide and 220 nm for the other 7 herbicides;
- The flow rate of the mobile phase was 1 mL/min and the gradient is presented in the table below.

Time (min)	A% (H ₂ O)	B% (ACN)	Curve
Initial	85	15	Initial
5	85	15	6
25	40	60	6
30	85	15	6
33	85	15	6

- **Linearity** - calibration curve, five concentration in the range 0.1 - 10 µg/mL of herbicide standards.
- **Limit of Detection (LOD)** - the lowest amount of herbicides in a sample which can be detected, under well-specified conditions, but not necessarily quantitated as an exact value.
- **Limit of Quantification (LOQ)** - the lowest amount of herbicides in a sample which can be quantitatively determined with suitable precision and accuracy.
- **Method Precision** - evaluated based on the relative standard deviation (SD) of the *intra-day precision (RSDr %)* and the *inter-day precision (RSDR %)*, both for standard solutions and spiked samples.
- **Recovery** - analysing spiked blank samples at the concentration of 2.5 mg/kg since there is no imposed concentration from European Commission. Codamix fertilizer was used as blank sample.

RESULTS AND DISCUSSIONS



Herbicide standard (up) and sample (down) chromatograms

Validation results

Parameter	Hexazinone	Simazine*	Simetryne	Atrazine	Ametryn	Propazine	Terbutylazine	Prometryn
Linearity	r=1.0000	r=1.0000	r=0.9999	r=1.0000	r=1.0000	r=1.0000	r=1.0000	r=1.0000
Cvx0 <10%	Cvx0 = 0.571	Cvx0 = 0.528	Cvx0 = 1.866	Cvx0 = 0.441	Cvx0 = 1.101	Cvx0 = 1.307	Cvx0 = 1.405	Cvx0 = 0.571
Standard solution verification (concentration 5 µg/mL for Hexazinone, 2.5 µg/mL for 7 Triazines)								
Average (µg/mL)	5.04	2.04	2.53	2.55	2.63	2.57	2.57	2.64
Accuracy (%)	100.90	81.47	101.08	102.03	105.10	102.76	102.64	105.44
BIAS (%)	0.90	-18.53	1.08	2.03	5.10	2.76	2.64	5.44
RSDr (%)	0.89	0.91	0.94	0.99	1.41	2.23	1.15	0.96
RSDR (%)	1.39	1.45	1.50	1.59	2.25	3.56	1.85	1.53
Spiked samples (concentration 5 µg/mL for Hexazinone, 2.5 µg/mL for 7 Triazine)								
Recovery (70 - 110%)	78.07	79.24	80.35	71.83	71.89	75.58	80.34	100.82
RSDr (%)	10.2	7.4	11.8	9.5	6.8	8.3	8.1	6.7
RSDR (%)	16.3	11.9	18.9	15.3	10.8	13.3	13.0	10.7
Uext (%)	30	30	30	30	30	30	30	30
Determined values of LOD and LOQ based on the developed method								
LOD (mg/kg)	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5
LOQ (mg/kg)	2	1	1	1	1	1	1	1
*Special consideration should be paid to Simazine due to difficulty of dissolution in solvent								

CONCLUSIONS

This method can be successfully used for determination of herbicides (Hexazinone, Simazine, Simetryne, Atrazine, Ametryn, Propazine, Terbutylazine, Prometryn) from lignosulfonate fertilizer matrix.

REFERENCES

- ISO 11264:2005 Soil quality - Determination of herbicides-Method using HPLC with UV-detection.
- EURACHEM Guide - The Fitness for Purpose of Analytical Methods (2014).

ACKNOWLEDGEMENTS

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