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# Quantification of BTEX in Soil by Headspace SPME–GC–MS Using Combined Standard Addition and Internal Standard Calibration

## Abstract

There is a great demand for simple, fast and accurate methods for quantification of volatile organic contaminants in soil samples. Solid-phase microextraction (SPME) has a huge potential for this purpose, but its application is limited by insufficient accuracy caused by a matrix effect. The aim of this research was to develop the method for BTEX quantification in soil using combined standard addition (SA) and internal standard (IS) calibration. Deuterated benzene (benzene-d<sub>6</sub>) was used as the internal standard for all analytes. The optimized method includes spiking replicate samples with different concentrations of BTEX standards and the same concentration of benzene-d<sub>6</sub>, equilibration of soil samples at 40 °C during 2 h, and SPME–GC–MS analysis. Precision and accuracy of IS and SA methods were compared on different soil matrices. Combined SA + IS method provided more precise calibration plots compared to the conventional SA calibration. The SA + IS calibration provided more precise and accurate results compared with a reference method based on solvent extraction followed by GC–MS when applied to BTEX quantification in real soil samples (spiked with diesel fuel and aged). Recoveries of BTEX from soil samples spiked with known concentrations of analytes using the developed method were in the range of 73–130% with RSD values less than 15% for all BTEX. The proposed simultaneous standard addition and internal standard approach can be advantageous and adopted for improved quantification of other toxic VOCs in soil.

## Keywords

SPME, BTEX quantification, Soil analysis, Matrix effect, Standard addition, Internal standard

## Disciplines

Agriculture | Biochemical and Biomolecular Engineering | Bioresource and Agricultural Engineering | Chemical Engineering

## Comments

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1           **Quantification of BTEX in soil by headspace SPME-GC-MS using combined standard**  
2                           **addition and internal standard calibration**

3  
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16  
17           **Abstract**

18           There is a great demand for simple, fast and accurate methods for quantification of volatile  
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22 standard addition (SA) and internal standard (SA+IS) calibration. Deuterated benzene was used as  
23 the internal standard for all analytes. The optimized method includes spiking of replicate samples  
24 with different concentrations of BTEX standards and the same concentration of benzene-*d*<sub>6</sub>,  
25 equilibration of soil samples at 40°C during 2 h, and SPME-GC-MS analysis. Precision and  
26 accuracy of IS and SA methods were compared using different soil matrices. Combined SA+IS  
27 method provided more precise calibration plots compared to the conventional SA calibration. The  
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32 RSD values less than 15% for all BTEX. Proposed simultaneous standard addition and internal

33 standard approach can be advantageous and adopted for improved quantification of other toxic  
34 VOCs in soil.

35  
36 **Keywords:** SPME; BTEX quantification; soil analysis; matrix effect; standard addition,  
37 internal standard.

38  
39 **1. Introduction**

40 Benzene, toluene, ethylbenzene and xylenes (BTEX) are a group of toxic volatile organic  
41 compounds (VOCs) considered human carcinogens and endocrine disruptors [1,2]. Soil pollution  
42 with BTEX can take place from numerous sources, including areas used for fuel extraction and  
43 transportation operations, refineries, gasification sites, and accidental releases. Spills of petroleum  
44 hydrocarbons cause serious soil and groundwater pollution that can affect environmental and food  
45 production systems. Quantification of BTEX in soils is important for providing environmental and  
46 food safety.

47 Sample preparation is the most crucial and limiting part of the analysis of VOCs in soil.  
48 Several sample preparation techniques are used for BTEX determination in soil, including purge-  
49 and-trap [3,4], headspace sampling [5–7], and solid-phase microextraction (SPME) [8–11]. SPME  
50 is a simple, fast, solventless method of sample preparation for VOCs in soil analysis, which is  
51 capable of full automation and on-site application [12].

52 Quantification of BTEX in soil using SPME is limited with a matrix effect caused by different  
53 extraction effectiveness of analyte from different soil samples. Main physicochemical soil  
54 properties affecting extraction effectiveness of BTEX are organic carbon and water content,  
55 particle size distribution and porosity [12]. Soil matrix effect is a source of greater uncertainties  
56 and inaccuracies in the whole process of analysis. To overcome this problem, matrix effect should  
57 either be: a) controlled using proper calibration methods that evaluate BTEX extraction  
58 effectiveness from every sample; or, b) decreased while facilitating improved extraction of BTEX.  
59 Techniques used for BTEX quantification in soil samples can include both approaches to overcome  
60 matrix effects (Table 1).

61

62 **Table 1.** Comparison of SPME-based techniques developed for BTEX quantification in soil

63

Sample preparation method	Calibration method	LOD, ng g <sup>-1</sup>	RSD, %	Reference
HS SPME (100 μm PDMS)	Standard addition	0.05-0.23	4-10	[8]
HS SPME (75μm CAR-PDMS)	Multiple HS-SPME + external standard	0.2-1.0	23-33	[9]
Internally-cooled SPME device (340 μm PDMS)	External standard	(1.2-3.2)×10 <sup>-4</sup>	-	[10]
UA-water-HS SPME (100 μm PDMS)	External standard	6.4-8.1	-	[11]
HS SPME (100 μm PDMS)	Internal standard (propylbenzene)	3-6	-	[13]
HS SPME	External standard in soil	8-20	5-8	[14]
UA-water-HS SPME (100 μm PDMS)	External standard in soil (matrix matched calibration)	2-20	-	[15]

64 Note: HS = headspace, UA = ultrasonic assisted, - = not reported

65

66 Approaches based on decreasing the matrix effect facilitate BTEX extraction using SPME  
67 fiber cooling, sample heating, the addition of water, and sonication of water-soil slurry (UA  
68 SPME). Calibration methods involving the control of matrix effect for quantification of BTEX in  
69 soils include standard addition (SA), internal standard (IS), and multiple HS-SPME. Advantages  
70 and disadvantages of each method were discussed in the recently published review [12]. Multiple  
71 SPME with Carboxen/polydimethylsiloxane (CAR-PDMS) coating can be applied for BTEX  
72 determination in soil providing a suitable extraction effectiveness of analytes. Multiple SPME has  
73 drawbacks such as a greater risk of analyte loss associated with multiple piercing of septa and  
74 increased time of sampling/sample preparation. SA calibration provides the most efficient matrix

75 effect control, but it is time-consuming, and its accuracy is highly dependent on concentrations  
76 range. IS calibration provides efficient matrix effect control, simple and fast operation. However,  
77 the main problem is a selection of a proper IS, which is very difficult taking into account many  
78 factors causing the matrix effect [12]. Isotopically-labeled ISs provide greatest accuracies, but they  
79 can be very costly and even unavailable for many analytes. Yang et al. [16] proposed the combined  
80 standard addition calibration with an internal standard (SA+IS) for the determination of tributyltin  
81 in sediment using SPME and GC-ICP-MS. This approach increased the accuracy of quantification  
82 of the analyte compared to a classic SA calibration; however, the method included preliminary  
83 extraction by acetic acid and derivatization, which are typically used for decreasing matrix effects.  
84 The SA+IS approach has never been applied for quantification of VOCs in soil using headspace  
85 SPME.

86 The aim of this work was to develop the method for BTEX quantification in soil by headspace  
87 SPME using the SA+IS calibration with deuterated benzene. The main hypothesis was that such  
88 approach provides the best combination of accuracy and speed of the BTEX quantification in soil  
89 samples. Optimization of equilibration of BTEX in different soil matrices was conducted to  
90 increase accuracy and precision of SA method.

91

## 92 **2. Experimental**

93

### 94 *2.1. Reagents and materials*

95 Benzene (99.9%), toluene (99.9%), ethylbenzene (99.8%), and *o*-xylene (97.0%) were  
96 purchased from Sigma-Aldrich (Germany). Methanol (HPLC grade) purchased from AppliChem  
97 (Germany) was used for the preparation of standard solutions. Benzene-*d*<sub>6</sub> (99.9%) (Sigma-  
98 Aldrich, Switzerland) was used as the internal standard. SPME fiber – 85 μm Carboxen/PDMS  
99 was obtained from Supelco (USA). Soil sampling and calibration were performed in 20 mL crimp-  
100 top headspace vials (HTA, Italy) with PTFE/silicone septa (Zhejiang Aijiren Technology Co.,  
101 China). All vials and septa were washed with distilled water and pre-conditioned at 140 °C for 2 h  
102 before analysis.

103

### 104 *2.2. Instrumentation*

105 Analyses were performed on the 6890N/5973N GC-MS system (Agilent, USA) equipped  
106 with Combi-PAL (CTC Analytics, Switzerland) SPME autosampler. Analytes were thermally

107 desorbed from SPME fibers in splitless mode at 240 °C. Chromatographic separation was  
108 conducted on a polar 60 m x 0.25 mm DB-WAXetr (Agilent, USA) column with 0.50 µm film  
109 thickness at constant helium (>99.995%, Orenburg-Tehgas, Russia) flow of 1.0 mL min<sup>-1</sup>. Oven  
110 temperature was programmed from initial 40 °C (held for 1 min) to 160 °C (held for 2 min), with  
111 a heating rate of 10 °C min<sup>-1</sup>. Temperatures of the ion source, quadrupole and MS interface were  
112 230, 150 and 240 °C, respectively. Detection was conducted using electron impact ionization at 70  
113 eV in selected ion monitoring (SIM) mode at m z<sup>-1</sup> of 78, 84, 91, 106, and 106 amu for selective  
114 detection and quantification of benzene, benzene-*d*6, toluene, ethylbenzene, and *o*-xylene,  
115 respectively. Dwell time of each ion was 50 ms.

116

### 117 *2.3. Samples*

118 Two different soil types were used: clay and soil with high humus content, with  
119 concentrations of humus of 0.90% and 45%, respectively. Both soils were collected near Almaty,  
120 Kazakhstan. Soils were cleaned from possible BTEX residues and water by heating in a drying  
121 furnace at 150 °C for 6 h.

122

### 123 *2.4 Methodology of experiments*

#### 124 *2.4.1 Study of effects of temperature and time on equilibration of BTEX and benzene-*d*6 in* 125 *different soil matrices*

126 Clean soil samples weighing 1.00 g were placed into a vial and spiked with BTEX and  
127 benzene-*d*6 standard solution to provide the final concentration of 100 ng g<sup>-1</sup>. High humus content  
128 soil samples were prepared with different water content (0, 5 and 25%) by the addition of water  
129 before spiking with BTEX. After spiking, vials were placed into the agitator of the autosampler to  
130 set desirable equilibration temperatures of 30, 40, or 50 °C. SPME was performed immediately  
131 after spiking and every 60 min until the complete stabilization of peak areas of all analytes. Every  
132 measurement was conducted from a different vial to avoid a signal decrease due to a sample  
133 depletion, analyte losses or sorption onto pierced septa, in three replicates. A total of 162 vials was  
134 used. Headspace SPME was conducted for 1.00 min at the studied equilibration temperature.

135

#### 136 *2.4.2 Study of a matrix effect control using benzene-*d*6 as IS*

137 Soil samples were prepared as described in section 2.4.1 and equilibrated at 40 °C for 4 h.  
138 SPME was conducted for 60 s at equilibration temperature (40 °C).

139

140 *2.4.3 Study of the effect of IS on the accuracy and precision of SA calibration*

141 Clean soil samples (section 2.3) weighing 100 g were spiked with 0.1 and 1.0 mL of diesel  
142 fuel taken from a commercial gas station in Almaty, Kazakhstan, and then aged in open beakers  
143 outside a window of the laboratory for 2 weeks to provide realistic conditions of soil contamination.

144 Analyses of aged soils spiked with diesel fuel were conducted using SA, and SA+IS  
145 approaches. For validation of obtained results, same soils were analyzed using solvent extraction  
146 before GC-MS determination of BTEX.

147 For SPME-GC-MS determination of BTEX using SA and combined SA+IS methods, soil  
148 samples of 0.2000-0.4000 g were placed in vials and spiked with 10  $\mu\text{L}$  of BTEX standard solutions  
149 with concentrations of all analytes 0, 10, 50 and 200  $\text{ng } \mu\text{L}^{-1}$ . The concentration of benzene-*d6* was  
150 same in all calibration samples – 10  $\text{ng } \text{g}^{-1}$ . After spiking, soil samples were equilibrated at 40 °C  
151 for 4 h. SPME was conducted at room temperature for 60 s using Carboxen/PDMS fiber. All  
152 experiments were conducted in two replicates.

153 For determination of BTEX using solvent extraction, calibration samples were prepared  
154 similarly to SPME calibration. After equilibration, analytes were extracted by 10 mL of organic  
155 solvent (methanol) and shaken for 10 min. Liquid part was then separated from soil and analyzed  
156 in direct injection of samples into GC-MS using SA approach.

157

158 *2.4.4 Validation of the optimized SPME-based method*

159 The optimized method was applied for quantification of BTEX in soil samples spiked with  
160 known concentrations. Two soil types and water contents (0 and 15%) were used. Spiking  
161 concentrations were 10, 100 and 500  $\text{ng } \text{g}^{-1}$ . Model soil samples were stored for 48 h before  
162 analysis. Calibration samples were prepared by addition of 10  $\mu\text{L}$  of standard solutions with BTEX  
163 concentrations 0, 1, 5 and 10  $\text{ng } \mu\text{L}^{-1}$  for soils with BTEX concentration 10  $\text{ng } \text{g}^{-1}$ ; 0, 5, 10 and 20  
164  $\text{ng } \mu\text{L}^{-1}$  for  $C = 100 \text{ ng } \text{g}^{-1}$ ; and 0, 10, 20 and 50  $\text{ng } \mu\text{L}^{-1}$  for  $C = 500 \text{ ng } \text{g}^{-1}$ . The concentration of  
165 benzene-*d6* was 1  $\text{ng } \mu\text{L}^{-1}$  in all spiked standard solutions. After spiking standard solutions, soil  
166 samples were equilibrated at 40 °C for 4 h, and extraction was conducted for 60 s at room  
167 temperature.

168



169 **3. Results and Discussion**

170

171 *3.1 Equilibration of BTEX in soils with different physicochemical properties*

172 Quantification using SA and IS calibrations requires spiking of soils with standards of  
173 analytes and an internal standard, respectively, followed by equilibration. Equilibration may be  
174 enhanced by the increase of temperature and/or addition of water [17]. The aim of this experiment  
175 was to establish time required for equilibration of spiked soils at different temperatures.  
176 Equilibration of BTEX in high humus content soil was accompanied by the decrease of analyte's  
177 recovery. This was likely due to a more uniform distribution of spiked standards into humus of  
178 soil sample that resulted in decreasing extraction effectiveness (Fig. 1). Temperature increase  
179 improved equilibration of soils after spiking BTEX standards. Equilibration at 30 and 40 °C was  
180 achieved in 2 h after spiking, and in just 1 h at 50 °C.

181

182 **Fig. 1.**

183

184 When equilibrated at 30 °C, peak areas of BTEX decreased by 46-48% during the first 2 h.  
185 When equilibrated at 40 °C, the peak area of benzene decreased by 20% from the initial value,  
186 toluene - by 40%, ethylbenzene and *o*-xylene – by 50%, respectively. When equilibrated at 50 °C,  
187 the response of benzene decreased by 10% from the initial value, toluene - by 25%, ethylbenzene  
188 and *o*-xylene – by 40%. Clearly, the largest improvement in BTEX recovery was made by gently  
189 increasing extraction temperature to 40 °C. Increasing temperature above 40 °C was not effective,  
190 most likely due to the well-documented offsetting effect of lower SPME effectiveness at a higher  
191 temperature.

192 Equilibration of BTEX in clay soils was reached immediately after spiking of standards at  
193 all temperatures (data not shown). Peak areas of analytes were stable within variability range of 1-  
194 5% between replicates and equilibration times. In contrast to the organic carbon-rich soil,  
195 temperature increase led to a reduction in peak areas of BTEX because extraction efficiency-  
196 limiting process is sorption of analytes onto SPME fiber, not the desorption from soil.

197 Water content affected equilibration of BTEX in soil (Fig. 2). Equilibration took longer for  
198 soil with 5% water content. For soils with 25% water content, equilibration took just 1 h after  
199 spiking. The precision of response (standard deviations of peak area) decreased with the increase  
200 of water content in the soil.

201 Equilibration plots for benzene-*d*6 were similar to benzene and toluene equilibration plots  
202 (Fig. A.1) because of their similar physicochemical properties. Thus, optimal temperature and time  
203 for equilibration of soils spiked with BTEX and benzene-*d*6 are 40 °C and 2 h, respectively.

204

205 **Fig. 2.**

206

### 207 *3.2 Matrix effect control of benzene-*d*6 as IS*

208 The internal standard approach can be used for controlling matrix effect during SPME of  
209 soils. In this case, the ratio of responses of the analyte and IS ( $S_a/S_{IS}$ ) is used as the analytical signal.  
210 At a constant analyte concentration, the  $S_a/S_{IS}$  ratio must be similar for any samples. The aim of  
211 this experiment was to establish whether benzene-*d*6 can be used as a reliable IS for quantification  
212 of BTEX in soil using SPME.

213 Soil carbon content affected the response ratio of BTEX and benzene-*d*6 (Fig. 3A). For  
214 benzene in soil with high humus content,  $S_a/S_{IS}$  was 30% higher than in clay soil. For TEX, having  
215 higher molecular weights than benzene-*d*6, the  $S_a/S_{IS}$  decreased with the increase of humus content  
216 in the soil. Values of  $S_{BTEX}/S_{IS}$  were 10, 65 and 100% higher in clay soils compared with high  
217 humus content soils for TEX, respectively.

218

219 **Fig. 3.**

220

221 Water content also affected  $S_a/S_{IS}$  (Fig. 3B). A response ratio of benzene and benzene-*d*6  
222 decreased with the increase of water content, while for other analytes that dependence was  
223 opposite. Change of BTEX and IS peak area ratios due to different water content (yet the same  
224 concentrations of analytes) was significant (30-35%). Thus, it can be concluded that benzene-*d*6  
225 is not a suitable internal standard for quantification of BTEX by internal standard calibration.  
226 Furthermore, the use of benzene-*d*6 does not even allow quantification of benzene by isotope  
227 dilution. This is likely because of great differences in molecular mass and physicochemical  
228 properties of benzene and benzene-*d*6.

229

230 *3.3 Combined standard addition and internal standard calibration for BTEX quantification*  
231 *in soils*

232 Both SA and IS calibrations have their advantages and drawbacks. Compared to IS, the SA  
233 calibration is a better approach for controlling matrix effects because a spiked analyte has the same  
234 properties as the analyte already present in the sample. However, the main problem of an SA  
235 calibration is caused by strict requirements to a method precision, which can be significantly  
236 improved using an IS calibration. Also, a minimal number of calibration samples to be made can  
237 be still decreased.

238 Thus, the scheme of the proposed method includes spiking of samples with different  
239 additions of BTEX standards and the same additions of benzene-*d*6, followed by equilibration of  
240 soil samples, and SPME-GC-MS analysis (Fig. 4). Such approach is very simple and can be easily  
241 automated. A similar approach was used by Yang et al. [16] for quantification of tributyltin by  
242 SPME-GC-ICP-MS, but our method does not require any extra additives and solvent extraction  
243 steps. Extraction is done immediately after soil equilibration.

244

245 **Fig. 4.**

246

247 *3.4 Effect of internal standard on the accuracy and precision of SA method*

248 The accuracy of an SA approach depends on the uncertainty of slope factor. The use of  $S_a/S_{IS}$   
249 as the analytical signal provided more precise calibration plots for determination of BTEX in soils  
250 (Fig. 5), particularly for benzene. For higher concentration range of benzene (Fig. 5A), relative  
251 standard deviations (RSDs) between slope factors (S) of two replicate calibration plots obtained by  
252 SA+IS calibration were two times lower than for SA calibration. For low benzene concentration,  
253 SA+IS approach provided an order of magnitude lower RSDs between slope factors. (Fig. 5B). For  
254 other analytes, SA+IS calibration also provided lower RSDs between slope factors (Figs. A.2-A.4).

255

256 **Fig. 5.**

257

258 When compared with a solvent extraction combined with GC-MS used as the reference  
259 method, the combined SA+IS approach provided most accurate results compared to SA and the IS  
260 (Table 2). Such results can be explained by a better precision of this approach.

261 Method validation on soil samples spiked with known concentrations of analytes provided  
 262 BTEX recoveries in the range of 73-130% (Table 3). Most recoveries ranged from 90 to 120%  
 263 meaning that the method fulfills requirements to the methods used in environmental monitoring.  
 264 Most accurate results were obtained for the highest studied concentration of 500 ng·g<sup>-1</sup>.

265  
 266 **Table 2.** Comparison of concentrations (ng g<sup>-1</sup>) and relative standard deviations between parallel  
 267 experiments obtained using SPME-GC-MS and SA, IS, SA+IS methods and solvent extraction  
 268 (SE+SA)

269

Analyte	SA		IS		SA+IS		SE+SA
	C, ng·g <sup>-1</sup>	RSD, %	C, ng·g <sup>-1</sup>	RSD, %	C, ng·g <sup>-1</sup>	RSD, %	C, ng·g <sup>-1</sup>
Benzene	1420	4.9	1550	11	1490	1.3	1500
Toluene	680	9.2	5500	40	600	0.1	610
Ethylbenzene	380	24	238	25	340	14	380
<i>o</i> -Xylene	173	2.4	290	9.3	205	6.1	380

270 Note: SE = solvent extraction

271

272 **Table 3.** Recoveries of BTEX quantification using simultaneous SA+IS approach

273

Soil type	Water content %	Spiked concentration ng·g <sup>-1</sup>	Measured concentration, ng·g <sup>-1</sup>				Recovery, %			
			B	T	E	X	B	T	E	X
Clay soil	0	10	11.0±1.6	12.1±1.2	9.2±1.5	11.8±0.3	110	121	92	118
		100	105±4	110±4	93±9	93±1	105	110	93	93
		500	497±4	520±7	496±2	509±1	99	104	99	102
	15	10	11.5±0.7	10.8±1.3	9.4±0.3	10.8±0.9	115	108	94	108
		100	92±5	73±4	104±10	108±15	92	73	104	108
		500	490±40	504±4	491±18	494±6	98	101	98	99
Organic soil	0	10	13±2	11.7±1.1	12.0±0.5	11.8±0.1	130	117	120	118
		100	107±1	112±3	98±1	94±4	107	112	98	94
		500	503±1	495±8	500±30	499±14	101	99	100	100
	15	10	10.5±1.2	12.4±0.6	11.7±0.1	11.7±0.1	105	124	117	117
		100	100±14	98±1	99±4	95±1	100	98	99	95
		500	491±15	509±7	506±2	499±4	98	102	101	100

274

275 Detection limits (LODs) of the developed method depend on extraction efficiencies of  
276 analytes from a particular sample. In this research, detection limits estimated using signal-to-noise  
277 ratio method were  $5 \text{ ng g}^{-1}$  for all BTEX in studied samples. Measuring lower BTEX concentrations  
278 can be possible by using longer extraction times. However, accuracy can be limited in the case of  
279 laboratory air pollution with BTEX. For example, in the case of analyte concentration in air  $100$   
280  $\mu\text{g m}^3$ ,  $19.5 \text{ mL}$  of headspace above soil sample can contain  $1.95 \text{ ng}$  of the analyte, which  
281 corresponds to the concentration of the analyte in soil  $1.95 \text{ ng g}^{-1}$ . If necessary, this problem can  
282 be solved by using a greater mass of soil sample in the vial or by purification of a laboratory air.  
283 In this research, concentrations of individual BTEX in laboratory air were always below  $50 \mu\text{g m}^3$ .

284

#### 285 **4. Conclusion**

286

287 This research reports on the first application of the simultaneous SA+IS approach for  
288 quantification of VOCs in soil using headspace SPME. BTEX compounds were used as model soil  
289 pollutants. Several practical lessons for adapting the SA+IS approach to a wider range of VOCs  
290 were learned. Standard addition and internal standard methods' accuracy and precision can be  
291 improved by a proper equilibration of soil samples after spiking standards. Time of BTEX  
292 equilibration in soils increased with the increase of organic carbon content in the soil. Benzene-*d*6  
293 cannot be recommended as an internal standard (IS) for quantification of BTEX in soil samples.  
294 However, benzene-*d*6 can be used to: (1) improve the precision of a standard addition (SA)  
295 approach by its addition to every analyzed sample at the same concentration, and (2) decrease the  
296 number of samples that must be analyzed for achieving the proper accuracy. Proposed method for  
297 BTEX quantification in soils provides reasonable accuracy (73-130 % recovery) and low RSD  
298 values (<15% for all BTEX). The use of simultaneous IS and SA approach allows to reduce the  
299 number of calibration samples and to increase the speed of analysis. New method improves on the  
300 Yang et al. [16] pioneering work for quantification of tributyltin by SPME-GC-ICP-MS, but our  
301 method does not require any extra additives and solvent extraction steps. Extraction is done  
302 immediately after soil equilibration.

303

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305

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368 **Figure captions:**

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371 **Fig. 1.** Effect of temperature (30, 40 and 50 °C) on equilibration of BTEX in soil. Conditions:  
372 soil type – high organic content soil; water content - 0%.

373

374 **Fig. 2.** Effect of water content (0, 5 and 25%) on equilibration of BTEX in soil. Conditions: soil  
375 type – high organic content soil; equilibration and extraction temperature 30 °C.

376

377 **Fig. 3.** Effect of soil type (A) and water content (B) on response ratio of BTEX and benzene-*d*6.  
378 Conditions: equilibration and extraction temperature 40 °C; A: water content 0%; B: soil type –  
379 high organic content soil.

380

381 **Fig. 4.** Scheme of the method for quantification of BTEX using combined standard addition and  
382 internal standard calibration.

383

384 **Fig. 5.** Calibration plots for quantification of benzene in soil with high organic carbon content by  
385 SA and SA+IS methods at high (A) and low (B) contamination level with diesel fuel.

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