Title
451085-02

Enforcement Method for Soil by LC-MS/MS

Metsulfuron-methyl (AE F075736)
Iodosulfuron-methyl-sodium (AE F115008)

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Completed On
04 Feb 2000

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OECD TIA 4.4.2

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Federal Republic of Germany

Study Identification

VOL. 63 of 229
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Date: March 20, 2000
GOOD LABORATORY PRACTICE STATEMENT

This report does not meet the requirements for 40 CFR Part 160, and differs in the following way:

1. Good Laboratory Practice Standards are not applicable to this report.

Sponsor/Submitter

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Manager, Regulatory Affairs

Date March 20, 2000
Notes

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APPROVALS PAGE

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date (d/m/y)

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SUMMARY

Enforcement Method for Soil by LC-MS/MS

Metsulfuron-methyl (AE F075736)
Iodosulfuron-methyl-sodium (AE F115008)

Relevant residue
Metsulfuron-methyl (AE F075736)
Iodosulfuron-methyl-sodium (AE F115008)

Test commodity
Two Soils: loamy sand and silty loam

Principle of the method
Residues of the sulfonylureas were extracted with acetonitrile / triethylamine 0.02 mol/L (4:1, v/v) from soil. After evaporation to dryness, the residues were reconstituted in water acidified with formic acid (0.01 mol/L). After a liquid/liquid extraction with ethyl acetate / formic acid (0.01 mol/L), the sulfonylureas were determined by LC-MS/MS.

The determination of the residues was done with matrix matched standards. To establish the calibration curve matrix test solutions were injected into the LC-MS/MS system.

Calibration
A curve of the form \( y = a + bx + cx^2 \) is applicable over the tested range of 0.1 to 5 ng/mL of matrix matched standards for the tested sulfonylureas.

Recovery efficiency, relative standard deviation (RSD)
Recovery experiments were conducted at 0.01 \( \mu g/kg \), 0.02 \( \mu g/kg \), 0.05 \( \mu g/kg \) and 0.5 \( \mu g/kg \) for two different soil types, a loamy sand and silty loam.

Validation results covering the requirements for enforcement methods were found for metsulfuron-methyl (AE F075736) and iodosulfuron-methyl-sodium (AE F115008) at the fortification levels of 0.02 \( \mu g/kg \), 0.05 \( \mu g/kg \) and 0.5 \( \mu g/kg \). Mean recoveries were found between 74 and 100 % at these fortification levels, with an RSD of 4 - 20 %.

It was demonstrated that also the level of 0.01 \( \mu g/kg \) could be detected. However this level does not completely fulfill the requirements of the validation of an analytical method. The apparent residues were found up to 0.006 \( \mu g/kg \) (\( \leq 0.3 \times \text{LOQ} \), \( \text{LOQ} = 0.02 \mu g/kg \)). The level of 0.02 \( \mu g/kg \) is therefore considered to be the appropriate limit of quantification for metsulfuron-methyl (AE F075736) and iodosulfuron-methyl-sodium (AE F115008).
### Summary table of recoveries:

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Soil type</th>
<th>Fortification level</th>
<th>Mean recovery [µg/kg]</th>
<th>RSD (a) [%]</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>AE F075736</td>
<td>Silty loam</td>
<td>0.01</td>
<td>81</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.02</td>
<td>82</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05</td>
<td>92</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>94</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Loamy sand</td>
<td>0.01</td>
<td>89</td>
<td>19</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.02</td>
<td>100</td>
<td>16</td>
<td>6</td>
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<tr>
<td></td>
<td></td>
<td>0.05</td>
<td>90</td>
<td>9</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>90</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>AE F115008</td>
<td>Silty loam</td>
<td>0.01</td>
<td>82</td>
<td>25</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.02</td>
<td>74</td>
<td>18</td>
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</tr>
<tr>
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<td></td>
<td>0.05</td>
<td>85</td>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>78</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Loamy sand</td>
<td>0.01</td>
<td>100</td>
<td>33</td>
<td>6</td>
</tr>
<tr>
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<td></td>
<td>0.02</td>
<td>90</td>
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<td>5</td>
</tr>
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<td></td>
<td>0.05</td>
<td>75</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>84</td>
<td>13</td>
<td>7</td>
</tr>
</tbody>
</table>

a) \[
\text{RSD} = \frac{\sum (R_i - R_m)^2}{n-1}^{1/2} \]

\( R_i \): recovery

\( R_m \): mean recovery

\( n \): number of recoveries

### Limit of quantification

The limit of quantification (LOQ) covering the requirements for metsulfuron-methyl (AE F075736), iodosulfuron-methyl-sodium (AE F115008) in soil was established and validated at 0.02 µg/kg.

### Specificity

Control samples of soils were analysed. The apparent residues were ≤ 0.006 µg/kg (≤ 0.3 * LOQ, LOQ = 0.02 µg/kg).

Due to the high specificity of MS/MS and the very low concentration analysed in soil, no further confirmation techniques are currently available.
Analytical method flow sheet

**Extraction sulfonyureas**

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 g soil</td>
<td>100 mL acetonitrile / triethylamine 0.02 mol/L (4:1, v/v)</td>
</tr>
<tr>
<td>Shake for 20 min. on the shaking machine or treat the sample for 2 min. with a desintegrator (the sample will be pulsed)</td>
<td></td>
</tr>
<tr>
<td>Centrifuge 5 min at 4000 rpm</td>
<td></td>
</tr>
<tr>
<td>Filter over cotton wool</td>
<td></td>
</tr>
<tr>
<td>Repeat with 100 mL acetonitrile / triethylamine 0.02 mol/L (4:1, v/v)</td>
<td></td>
</tr>
<tr>
<td>Combine the organic phases</td>
<td>Reduce to dryness using a vacuum rotary evaporator (bath temperature ca. 60 °C)</td>
</tr>
</tbody>
</table>

**Clean up**

**Liquid/liquid extraction**

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolve the residue in 20 mL fomric acid (0.01 mol/L water) using an ultrasonic bath</td>
<td></td>
</tr>
<tr>
<td>Transfer the solution in the Falcon beaker and centrifuge (5 min at 4000 rpm)</td>
<td></td>
</tr>
<tr>
<td>Repeat the first step with 10 mL formic acid (0.01 mol/L water)</td>
<td></td>
</tr>
<tr>
<td>Wash the round bottom flask with 15 mL ethyl acetate</td>
<td></td>
</tr>
<tr>
<td>Transfer the ethyl acetate into the centrifuge beaker (Falcon beaker)</td>
<td></td>
</tr>
<tr>
<td>Shake hardy</td>
<td></td>
</tr>
<tr>
<td>Centrifuge for 5 min at 4000 rpm</td>
<td></td>
</tr>
<tr>
<td>Transfer the ethyl acetate into the separatory funnel</td>
<td></td>
</tr>
<tr>
<td>Shake the formic acid (0.01 mol/L water) / ethyl acetate mixture for 1 min</td>
<td></td>
</tr>
<tr>
<td>Transfer the formic acid phase into a second separatory funnel</td>
<td></td>
</tr>
<tr>
<td>Give the ethyl acetate phase into a 100 mL round bottom flask</td>
<td></td>
</tr>
<tr>
<td>Repeat extraction of the formic acid twice with 15 mL ethyl acetate, each</td>
<td></td>
</tr>
<tr>
<td>Combine the ethyl acetate phases and reduce to dryness using a vacuum rotary evaporator (bath temperature ca. 60 °C).</td>
<td></td>
</tr>
</tbody>
</table>

**LC-MSMS**

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolve in acetonitrile / water (1 : 1, v/v)</td>
<td>final volume should be 2.0 mL to 10.0 mL</td>
</tr>
<tr>
<td>(If necessary filter the final solution over an injection filter (0.45 μm))</td>
<td>LC-MS/MS</td>
</tr>
</tbody>
</table>
1 Organization and Personnel

Sponsor: AgrEvo GmbH
D - 65926 Frankfurt am Main

Test facility: AgrEvo GmbH
Rückstände und Verbrauchersicherheit
D - 65926 Frankfurt am Main
Head: Dr. M. Uihlein

Study director: Dr. A. Wrede
Address: see Test facility

Method No.: EM F13/99-0
2 Objectives
The objective of this study is the development of a multi-residue method for the determination of residues of sulfonyleureas, e.g. metsulfuron-methyl (AE F075736), iodosulfuron-methyl-sodium (AE F115008), in soil by LC-MS/MS.

3 Test commodities
For development of the analytical method two different types of soil from the field dissipation study ER 98 EUR 500 were used. One soil, a loamy sand (0.80 % org. C, pH 7.5), was from the field trial (I98001R) in Italy, the other soil, a silty loam (1.38 % org. C, pH 7.4), was from the field trial (S98001R) in Spain.

4 Relevant residue and reference substances
4.1 Relevant residue
The relevant residues consist of the parent compounds metsulfuron-methyl (AE F075736) and iodosulfuron-methyl-sodium (AE F115008).
4.2 Test and reference substances

Metsulfuron-methyl (AE F075736)

Chemical name (IUPAC): methyl 2-[3-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl) ureidosulfonyl]-benzoate

Empirical formula: C_{14}H_{16}N_{5}O_{6}S

Molecular weight: 381.4

Structural formula:

Certificate of analysis: AZ 06892
Drawn up by: Hoechst Schering AgrEvo GmbH
Produktanalytik
D-65926 Frankfurt am Main, Germany

Purity: 98.4 % (w/w)

Expiry date (d/m/y): 07 May 2000
Iodosulfuron-methyl-sodium (AE F115008)

Chemical name (IUPAC): methyl 4-iodo-2-{3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)ureidosulfonyl}benzoate, sodium salt

Empirical formula: C_{16}H_{13}IN_{3}NaO_{6}S

Molecular weight: 529.3

Solubility (20 °C):

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>&gt; 380 g/L</td>
<td>ref. 1</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>&gt; 500 g/L</td>
<td>ref. 1</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>23 g/L</td>
<td>ref. 1</td>
</tr>
<tr>
<td>n-hexane</td>
<td>1.2 * 10^{-3} g/L</td>
<td>ref. 1</td>
</tr>
<tr>
<td>methanol</td>
<td>12 g/L</td>
<td>ref. 1</td>
</tr>
<tr>
<td>n-heptane</td>
<td>1.1 * 10^{-3} g/L</td>
<td>ref. 1</td>
</tr>
<tr>
<td>2-propanol</td>
<td>4.4 g/L</td>
<td>ref. 1</td>
</tr>
<tr>
<td>toluene</td>
<td>2.1 g/L</td>
<td>ref. 1</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>52 g/L</td>
<td>ref. 1</td>
</tr>
<tr>
<td>DMSO</td>
<td>&gt; 500 g/L</td>
<td>ref. 1</td>
</tr>
<tr>
<td>PEG</td>
<td>87 g/L</td>
<td>ref. 1</td>
</tr>
</tbody>
</table>

Structural formula:

Certificate of analysis: AZ 07931
Drawn up by: Hoechst Schering AgrEvo GmbH Produktanalytik D-65926 Frankfurt am Main, Germany

Purity: 97.3 % (w/w)
Expiry date (d/m/y): 30 May 2000
5 Procedures

5.1 Principle of Analytical Method

The method flow sheet is presented in Annex I.

Residues of the sulfonylureas were extracted with acetonitrile / triethylamine 0.02 mol/L (4:1, v/v) from soil. After evaporation to dryness, the residues were reconstituted in water acidified with formic acid (0.01 mol/L). After a liquid/liquid extraction with ethyl acetate / formic acid (0.01 mol/L), the sulfonylureas were determined by LC-MS/MS.

The determination of the residues was done with matrix matched standards. To establish the calibration curve matrix test solutions were injected into the LC-MS/MS-system.

5.2 Reagents

- acetonitrile Chromasolv p.A. (Riedel-de Haën, Germany)
- triethylamine, 0.02 mol/L
- formic acid, 0.01 mol/L
- ethyl acetate Pestanal (Riedel-de Haën, Germany)
- AE F075736, analytical standard (AgrEvo GmbH, Germany)
- AE F115008, analytical standard (AgrEvo GmbH, Germany)

Stock solutions of the analytical standards were prepared by dissolving about 50 mg of analytical standard of AE F075736 and AE F115008 in ca. 50 mL acetonitrile / triethylamine (0.02 mol/L), 4:1, v/v. Concentration of the stock solutions was 1.0 mg/mL. Working solutions were prepared from the stock solution by further dilution with acetonitrile / water, 1:1, v/v. The working solutions contain all needed analytical standards.

5.3 Apparatus

The following list contains the apparatus used in the laboratory of the author for method development and validation. Suitable alternatives can be taken.

- standard laboratory glassware
- rotary vacuum evaporator with water bath
- centrifuge tube
- ultrasonic bath
- centrifuge (e.g. Heraeus Labofuge GL with rotor)
- Ultraturrax Typ 18/10
- LC-MS/MS system Quattro LC-Z (Micromass) (see section 5.6)
- chromatography column, Hypersil BDS, 5 µm, 250 mm x 3 mm
5.4 Preparation of samples and storage
Sample handling and preparation of the samples should be done following procedures mentioned in the relevant guidelines.
Soil samples should be mixed thoroughly and were stored deep-frozen.

5.5 Laboratory Steps

5.5.1 Extraction
Weigh 50 g of the homogenised soil sample into a centrifuge beaker. Fortify at this stage for recovery experiments. Add 100 mL acetonitrile / triethylamine 0.02 mol/L (4:1, v/v). Shake for 20 min. on the shaking machine or treat the sample for 2 min. with a desintegrator (the sample will be pulsed).
Centrifuge the mixture for 5 min at 4000 rpm and give the liquid phase into a 500 mL round bottom flask via a funnel with cotton wool. Repeat the extraction with 100 mL acetonitrile / triethylamine 0.02 mol/L (4:1, v/v).
Combine the extracts. Reduce to dryness using a vacuum rotary evaporator (bath temperature ca. 60 °C).

5.5.2 Liquid-liquid clean-up
Dissolve the residue in 20 mL formic acid (0.01 mol/L water) using an ultrasonic bath.
Transfer the solution in the centrifuge beaker (Falcon beaker) and centrifuge (5 min at 4000 rpm). Transfer the solution into a 100 mL separation funnel. Repeat the first step with 10 mL formic acid (0.01 mol/L water).
Wash the round bottom flask with 15 mL ethyl acetate, transfer the ethyl acetate into the centrifuge beaker (Falcon beaker). Shake hard. Centrifuge for 5 min at 4000 rpm. Transfer the ethyl acetate into the separation funnel filled with the 30 mL formic acid (see above).
Shake the formic acid (0.01 mol/L water) / ethyl acetate mixture for 1 min. Transfer the formic acid phase into a second separatory funnel. Give the ethyl acetate phase into a 100 mL round bottom flask. Repeat extraction of the formic acid twice with 15 mL ethyl acetate, each. Combine the ethyl acetate phases and reduce to dryness using a vacuum rotary evaporator (bath temperature ca. 60 °C).
(In the case of bad separation, combine the ethyl acetate phases with the mixed phases into a centrifuge beaker (Falcon beaker). Centrifuge the mixture for 1 min at 4000 rpm. Transfer the aqueous phase to waste using a 10 mL single syringe stainless steel cannula. Transfer the ethyl acetate phase into a round bottom flask. Reduce to dryness using a vacuum rotary evaporator (bath temperature ca. 60 °C).)
Dissolve the residue in acetonitrile / water (1 : 1; v/v). The final volume should be 2.0 to 10.0 mL. This solution is ready for quantification with LC-MS/MS. If necessary filter the final solution over an injection filter (0.45 μm).
5.5.3 Matrix calibration

To 900 μL matrix solution 100 μL of a test solution with known amounts of sulfonylureas, e.g. metosulfuron-methyl (AE F075736) and iodosulfuron-methyl-sodium (AE F115008), was added. This gives a final volume of 1 mL. If smaller volumes were needed, aliquots of the matrix solution and test solution were used. However, the ratio matrix solution / test solution should be 9 : 1. For the matrix solutions a worked up control sample, diluted in acetonitrile / water (1 : 1; v/v) was used. To establish a calibration curve matrix test solutions were injected into the LC-MS/MS-system.

5.6 Determination of residues

The following conditions have been used successfully during validation of this analytical method. If different equipment and columns are used, modifications of the given conditions may be necessary.

HPLC-conditions

| Column: | Hypersil BDS, 5 μm, 250 mm x 3 mm |
| Column temperature: | 30 °C |
| Injection volume: | 50 μL |
| Flow: | 0.25 mL / min |
| Pump A: | Formic acid 0.01 mol/L |
| Pump B: | Acetonitrile |

Gradient

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>20</td>
</tr>
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<td>13</td>
<td>20</td>
<td>80</td>
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<td>20</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>22</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>27</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

MS/MS Conditions

Analytical standards of all compounds should be taken to determine the most sensitive mass-transition from parent to daughter ion. Afterwards all relevant parameters of the MS/MS-system have to be optimized regarding a maximum sensitivity. Tabulated values below were chosen during this validation study but may vary depending on the system used.

To minimize contamination of the MS/MS system the capillary outlet behind the HPLC-column was connected to a switch valve. This construction ensures that only the flow within a certain time window (expected retention time ± ca. 1.5 min) enters the system while the rest is discarded. During the discarding phase the MS/MS system is stabilised with a flow of 0.25 mL/min of formic acid 0.01 mol/L / Acetonitrile (1 : 1, v/v), provided by an additional HPLC pump.
Tune parameter MS/MS

Modus: MRM; Electrospray positive
Capillary: 3.50 kV
Extractor: 2 V
RF Lens: 0.20 V
Source block temp: 150 °C
Desolvation temp.: 350 °C
Nebuliser gas: ca. 90 L/h
Drying gas: ca. 600 L/h

Analyser:
LM Res 1: 10.0
HM Res 1: 10.0
I Energy 1: 1.0 V
Entrance: 10
Exit: 15
LM Res 2: 15.0
HM Res 2: 15.0
I Energy 2: 2.0 V
Multiplier: 650 V

Scanning method

<table>
<thead>
<tr>
<th>Substance</th>
<th>Parent [m/z]</th>
<th>Daughter [m/z]</th>
<th>Dwell [s]</th>
<th>Coll. Energy</th>
<th>Cone Voltage [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AE F075736</td>
<td>382.20</td>
<td>167.00</td>
<td>0.3</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>AE F115008</td>
<td>508.20</td>
<td>167.00</td>
<td>0.3</td>
<td>20</td>
<td>23</td>
</tr>
</tbody>
</table>

Retention time

<table>
<thead>
<tr>
<th>Substance</th>
<th>Retention time [min]</th>
<th>Detection time windows [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AE F075736</td>
<td>16.9</td>
<td>14.5 – 20.5</td>
</tr>
<tr>
<td>AE F115008</td>
<td>18.9</td>
<td>14.5 – 20.5</td>
</tr>
</tbody>
</table>
5.6.1 MS spectrum of AE F075736

Parent scan

Daughter scan
5.6.3 MS spectrum of AE F115008

Parent scan

Daughter scan
5.7 Calibration

The concentrations of the tested sulfonylureas were calculated using external standards at 5 - 6 different concentrations over a range from 0.1 pg/µL up to 5 pg/µL. The recommended order of samples / test solutions for setting up a sequence for LC-MS/MS-determination is 'test solution – sample – sample – test solution'. If different equipment is used and/or more or less samples are worked up, modifications of this order may be necessary.

5.8 Calculations

**Determination of concentration of the analytical target in the final solution**

The concentrations of the analytes in control samples, fortified samples and treated samples were calculated using external standard procedures with multi level or single level calibration.

**Single level calibration (one point calibration):**

\[
C_S = \frac{P_S}{P_R} \cdot C_R \cdot \frac{I_R}{T_4} \quad \left[ \frac{\text{ pg/µL}}{\text{ counts}} = \frac{\text{ counts}}{\text{ pg/µL}} \cdot \frac{\text{ µL}}{\text{ µL}} \right]
\]

- \(C_S\): Concentration in final sample solution \( V_{\text{end}} \) (identical with conc. in \( T_4 \)) (treated, untreated and recovery)
- \(C_R\): Concentration in reference solution
- \(P_S\): Peak area or peak height of the sample solution
- \(P_R\): Peak area or peak height of the reference solution
- \(T_4\): Injection volume of the sample solution
- \(I_R\): Injection volume of the reference solution

**Multi level calibration (calibration curve):**

For the calibration peak areas (heights) of the standards were plotted versus the corresponding concentrations. An optimized calibration curve of the following form

\[
f(C_S) = P = a + bC_S + cC_S^2
\]

is calculated, where \(f(C_S)\) is the peak area (height), \(C_S\) the concentration of the analyte in the final sample extract and \(a, b, c\) are constants.
Determination of residues
Calculation of residues was carried out by a data handling software according to the following procedure

\[
\text{Res} = \frac{C_s \cdot V_{\text{end}} \cdot f}{W \cdot 1000}
\]

\[mg/kg = \frac{(ng/mL) \cdot mL \cdot 1}{g \cdot 1000}\] (3)

\[
f = \frac{V_1 \cdot V_2 \cdot V_n}{T_1 \cdot T_2 \cdot T_n}
\]

\[
1 = \frac{mL \cdot mL \cdot mL}{mL \cdot mL \cdot mL}
\] (4)

\begin{align*}
\text{Res} & \quad \text{Residue} \quad [mg/kg] \\
C_s & \quad \text{Concentration in final sample solution \(V_{\text{end}}\) (treated, untreated and recovery)} \quad [ng/mL] \\
W & \quad \text{Sample weight} \quad [g] \\
f & \quad \text{Dilution factor} \quad \text{without dimension} \\
V_1 & \quad \text{Volume for primary extraction} \quad [mL] \\
V_2 & \quad \text{Volume after making up of aliquot \(T_1\)} \quad [mL] \\
V_n & \quad \text{Volume after making up of aliquot \(T_{n-1}\) (\(n = 3, 4\) and so on)} \quad [mL] \\
V_{\text{end}} & \quad \text{Final sample solution (identical with \(V_2\) or \(V_3\) or \(V_n\) depending on the method)} \quad [mL] \\
T_1 & \quad \text{Aliquot of \(V_1\)} \quad [mL] \\
T_2 & \quad \text{Aliquot of \(V_2\)} \quad [mL] \\
T_n & \quad \text{Aliquot of \(V_n\) (\(n = 3, 4\) and so on)} \quad [mL]
\end{align*}

Determination of recovery rates
Calculation of recovery rates were carried out by a data handling software according to the following procedure

\[
\text{Res}_{\text{d}} = \text{Res}_{\text{(Rec)}} - \text{Res}_{\text{(Unt)}}
\]

\[
\text{Rec} = \frac{\text{Res}_{\text{d}} \cdot 100}{\text{Res}_f}
\]

\[\% = \frac{mg/kg \cdot \%}{mg/kg}\] (5)

\[\% = \frac{mg/kg \cdot \%}{mg/kg}\] (6)

\begin{align*}
\text{Res}_{\text{(Rec)}} & \quad \text{Residue in the sample solution of the recovery test calculated with} \quad [mg/kg] \\
\text{Res}_{\text{(Unt)}} & \quad \text{Residue in the sample solution of the corresponding untreated control} \quad [mg/kg] \\
\text{Rec} & \quad \text{Recovery rate} \quad [\%] \\
\text{Res}_f & \quad \text{Concentration spiked for fortification} \quad [mg/kg] \\
\text{Res}_g & \quad \text{Concentration detected by analytical method} \quad [mg/kg]
\end{align*}
6 Results

6.1 Recoveries

For the validation of the analytical method of metsulfuron-methyl (AE F075736) and iodosulfuron-methyl-sodium (AE F115008) in soil, recovery experiments were conducted at 0.01 μg/kg, 0.02 μg/kg, 0.05 μg/kg and 0.5 μg/kg. At each level for each compound 5 - 13 recovery values were determined.

Validation results covering the requirements for enforcement methods were found for metsulfuron-methyl (AE F075736) and iodosulfuron-methyl-sodium (AE F115008) at the fortification levels of 0.02 μg/kg, 0.05 μg/kg and 0.5 μg/kg. For AE F075736 the mean recoveries were found between 82 and 100 % at fortification levels of 0.02 - 0.5 μg/kg, with an RSD of 6 - 18 %. For AE F115008 the mean recoveries were found between 74 and 90 % at fortification levels of 0.02 - 0.5 μg/kg, with an RSD of 4 - 20 %.

It was demonstrated that also the level of 0.01 μg/kg could be detected. However this level do not completely fulfil the requirements of the validation of an analytical method. The apparent residue were found in some cases also between 0.03 μg/kg and 0.06 μg/kg, an apparent residue only below 0.006 μg/kg (≤ 0.3 * LOQ, LOQ = 0.02 μg/kg) seems to be reachable. The level of 0.02 μg/kg is therefore considered to be the appropriate limit of quantification for metsulfuron-methyl (AE F075736) and iodosulfuron-methyl-sodium (AE F115008).

Recoveries are calculated with calibration curves of matrix matched standards according to the procedure described in section 5.8 with correction for apparent residues.

Control samples of soils were analysed. The apparent residues were ≤ 0.006 μg/kg (≤ 0.3 * LOQ, LOQ = 0.02 μg/kg). For details see appendix II.

A summary of all recoveries for metsulfuron-methyl (AE F075736) and iodosulfuron-methyl-sodium (AE F115008) are given in the following table.
Summary table of recoveries:

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Soil type</th>
<th>Fortification level [µg/kg]</th>
<th>Mean recovery [%]</th>
<th>RSD (a) [%]</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>AE F075736</td>
<td>Silty loam</td>
<td>0.01</td>
<td>81</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.02</td>
<td>82</td>
<td>18</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05</td>
<td>92</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>94</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Loamy sand</td>
<td>0.01</td>
<td>89</td>
<td>19</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.02</td>
<td>100</td>
<td>16</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05</td>
<td>90</td>
<td>9</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>90</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>AE F115008</td>
<td>Silty loam</td>
<td>0.01</td>
<td>82</td>
<td>25</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.02</td>
<td>74</td>
<td>18</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05</td>
<td>85</td>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>78</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Loamy sand</td>
<td>0.01</td>
<td>100</td>
<td>33</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.02</td>
<td>90</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05</td>
<td>75</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>84</td>
<td>13</td>
<td>7</td>
</tr>
</tbody>
</table>

The calculation was done with calibration function of peak areas.

\[ \text{RSD} = \frac{\text{S.D.}}{\text{Mean Recovery}} \times 100 \%
\]

\[ \text{S.D.} = \left( \frac{\sum (R_i - \bar{R}_o)^2}{n - 1} \right)^{1/2} \]

\[ R_i: \text{recovery} \]
\[ \bar{R}_o: \text{mean recovery} \]
\[ n: \text{number of recoveries} \]

6.2 Limit of Quantification (LOQ)

The lowest level at which metsulfuron-methyl (AE F075736) and iodosulfuron-methyl-sodium (AE F115008) have been quantified in this study and show valid results is 0.02 µg/kg in soil. This level is therefore considered to be the appropriate limit of quantification for metsulfuron-methyl (AE F075736) and iodosulfuron-methyl-sodium (AE F115008).

6.3 Blank values

Analysis of control samples has shown that apparent residues observed were n.d. (non detectable, < 0.3 x LOQ, LOQ = 0.02 µg/kg). This demonstrates that 0.02 µg/kg are the feasible levels for recognition of residues with reasonable certainty.

6.4 Specificity

Due to the high specificity of MS/MS and the very low concentration analysed in soil, no further confirmation techniques are currently available.
6.5 Critical steps of the method
- Check the pH-value at „Liquid-liquid clean-up" before adding ethyl acetate. The pH-value must be 3 to 4. At lower pH-values the sulfonyleurases can decompose.
- End the evaporation of the „Liquid-liquid clean-up" immediately after reaching dryness.
- Because of the very low LOQ, take care for a contamination of the samples.

6.6 Time for analysis
From extraction of the soil samples to preparation of the final solutions for LC-MS/MS determination, it is normally possible to analyse a batch of 12 samples in one day.
<table>
<thead>
<tr>
<th>No</th>
<th>Doc No</th>
<th>Report No</th>
<th>Author(s)</th>
<th>Title</th>
<th>Source and Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A54684</td>
<td>CP 94/070</td>
<td>Sadowsky-Dunkmann I., Schmidt W., 1995</td>
<td>Substance, pure</td>
<td>Code: HOE 115008 00 ZB97 0001</td>
</tr>
</tbody>
</table>
## Annex I: Analytical method flow sheet

### Extraction sulfonylureas

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>50 g soil</td>
</tr>
<tr>
<td>2.</td>
<td>100 mL acetonitrile / triethylamine 0.02 mol/L (4:1, v/v)</td>
</tr>
<tr>
<td>3.</td>
<td>Shake for 20 min. on the shaking machine or treat the sample for 2 min. with a desintegrator (the sample will be pulsed)</td>
</tr>
<tr>
<td>4.</td>
<td>Centrifuge 5 min at 4000 rpm</td>
</tr>
<tr>
<td>5.</td>
<td>Filter over cotton wool</td>
</tr>
<tr>
<td>6.</td>
<td>Repeat with 100 mL acetonitrile / triethylamine 0.02 mol/L (4:1, v/v), combine the organic phases</td>
</tr>
<tr>
<td>7.</td>
<td>Reduce to dryness using a vacuum rotary evaporator (bath temperature ca. 60 °C)</td>
</tr>
</tbody>
</table>

### Clean up

- **Liquid/Liquid Extraction**
- **Ethyl acetate / formic acid**

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Dissolve the residue in 20 mL formic acid (0.01 mol/L water) using an ultrasonic bath</td>
</tr>
<tr>
<td>2.</td>
<td>Transfer the solution in the Falcon beaker and centrifuge (5 min at 4000 rpm)</td>
</tr>
<tr>
<td>3.</td>
<td>Repeat the first step with 10 mL formic acid (0.01 mol/L water)</td>
</tr>
<tr>
<td>4.</td>
<td>Wash the round bottom flask with 15 mL ethyl acetate</td>
</tr>
<tr>
<td>5.</td>
<td>Transfer the ethyl acetate into the centrifuge beaker (Falcon beaker)</td>
</tr>
<tr>
<td>6.</td>
<td>Shake hardly</td>
</tr>
<tr>
<td>7.</td>
<td>Centrifuge for 5 min at 4000 rpm</td>
</tr>
<tr>
<td>8.</td>
<td>Transfer the ethyl acetate into the separatory funnel</td>
</tr>
<tr>
<td>9.</td>
<td>Shake the formic acid (0.01 mol/L water) / ethyl acetate mixture for 1 min</td>
</tr>
<tr>
<td>10.</td>
<td>Transfer the formic acid phase into a second separatory funnel</td>
</tr>
<tr>
<td>11.</td>
<td>Give the ethyl acetate phase into a 100 mL round bottom flask</td>
</tr>
<tr>
<td>12.</td>
<td>Repeat extraction of the formic acid twice with 15 mL ethyl acetate, each</td>
</tr>
<tr>
<td>13.</td>
<td>Combine the ethyl acetate phases and reduce to dryness using a vacuum rotary evaporator (bath temperature ca. 60 °C).</td>
</tr>
</tbody>
</table>

### LC-MSMS

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Dissolve in acetonitrile / water (1:1, v/v)</td>
</tr>
<tr>
<td>2.</td>
<td>Final volume should be 2.0 to 10.0 mL</td>
</tr>
<tr>
<td>3.</td>
<td>(if necessary filter the final solution over an injection filter (0.45 μm))</td>
</tr>
<tr>
<td>4.</td>
<td>LC-MS/MS</td>
</tr>
</tbody>
</table>
Annex II: Typical calibration curves

Typical calibration curves given on the following pages. These are curves of matrix matched standards (matrix soil).
$y = B^*x + C^*x^2$, Weighting: None

A: 0.00000
B: 32.61109
C: 0.00661

<table>
<thead>
<tr>
<th>Int. Standard</th>
<th>Menge(exp)</th>
<th>Sign.(exp)</th>
<th>Sign.(ber)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>pg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1001</td>
<td>10</td>
<td>320</td>
<td>327</td>
</tr>
<tr>
<td>1002</td>
<td>5</td>
<td>153</td>
<td>163</td>
</tr>
<tr>
<td>1003</td>
<td>5</td>
<td>180</td>
<td>163</td>
</tr>
<tr>
<td>1004</td>
<td>10</td>
<td>373</td>
<td>327</td>
</tr>
<tr>
<td>1005</td>
<td>25</td>
<td>873</td>
<td>819</td>
</tr>
<tr>
<td>1006</td>
<td>25</td>
<td>835</td>
<td>819</td>
</tr>
<tr>
<td>1007</td>
<td>50</td>
<td>1698</td>
<td>1647</td>
</tr>
<tr>
<td>1008</td>
<td>50</td>
<td>1987</td>
<td>1647</td>
</tr>
<tr>
<td>1009</td>
<td>100</td>
<td>3138</td>
<td>3327</td>
</tr>
<tr>
<td>1010</td>
<td>100</td>
<td>3223</td>
<td>3327</td>
</tr>
<tr>
<td>1011</td>
<td>250</td>
<td>6321</td>
<td>8568</td>
</tr>
<tr>
<td>1012</td>
<td>250</td>
<td>7841</td>
<td>8568</td>
</tr>
</tbody>
</table>

Sidebew: 356
Fehler-Summe: -243
$y = B \cdot x + C \cdot x^2$, Weighting: None

A: 0.000000
B: 28.89490
C: 0.00755

<table>
<thead>
<tr>
<th>inL Standard</th>
<th>Menge(exp)</th>
<th>Sign.(exp)</th>
<th>Sign.(ber)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>PG</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1001</td>
<td>10</td>
<td>307</td>
<td>290</td>
</tr>
<tr>
<td>1002</td>
<td>5</td>
<td>158</td>
<td>145</td>
</tr>
<tr>
<td>1003</td>
<td>5</td>
<td>189</td>
<td>145</td>
</tr>
<tr>
<td>1004</td>
<td>10</td>
<td>357</td>
<td>290</td>
</tr>
<tr>
<td>1005</td>
<td>25</td>
<td>717</td>
<td>727</td>
</tr>
<tr>
<td>1006</td>
<td>25</td>
<td>724</td>
<td>727</td>
</tr>
<tr>
<td>1007</td>
<td>50</td>
<td>1277</td>
<td>1454</td>
</tr>
<tr>
<td>1009</td>
<td>100</td>
<td>2794</td>
<td>2965</td>
</tr>
<tr>
<td>1010</td>
<td>100</td>
<td>3247</td>
<td>2965</td>
</tr>
<tr>
<td>1012</td>
<td>250</td>
<td>7685</td>
<td>7685</td>
</tr>
<tr>
<td>Stdev:</td>
<td>137</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fehler-Summe:</td>
<td>-43</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Blindwertabzug U002: 0 counts
Annex III: Typical chromatograms

The electronic plots of chromatograms presented on the following pages show the peak height in counts plotted vs. the retention time in minutes. Examples of typical chromatograms are presented in the following order:

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Lab code</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silty loam</td>
<td>I004</td>
<td>Test 10 pg /Injection of AE F075736, AE F115008 Matrix: silty loam</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>R032</td>
<td>Recovery 0.02 µg/kg of AE F075736, AE F115008 Matrix: silty loam</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>R001</td>
<td>Recovery 0.05 µg/kg of AE F075736, AE F115008 Matrix: silty loam</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>U001</td>
<td>Control Matrix: silty loam</td>
<td>34</td>
</tr>
<tr>
<td>Loamy sand</td>
<td>I013</td>
<td>Test 10 pg /Injection of AE F075736, AE F115008 Matrix: loamy sand</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>R041</td>
<td>Recovery 0.02 µg/kg of AE F075736, AE F115008 Matrix: loamy sand</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>R017</td>
<td>Recovery 0.05 µg/kg of AE F075736, AE F115008 Matrix: loamy sand</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>U003</td>
<td>Control Matrix: loamy sand</td>
<td>38</td>
</tr>
</tbody>
</table>
Soy type | Lab code | Description | Matrix: silty loam
---|---|---|---
Silty loam | I004 | Test | 10 pg /Injection of AE F075736, AE F115008

Sample List: C:\data\AE F075032\CR99032.PRO\SampleDB\sch001
Last modified: Fri Dec 03 08:58:09 1999
Method: C:\data\AE F075032\CR99032.PRO\Method\EM F13990
Last modified: Fri Nov 12 07:28:31 1999

- Name: I004
- Text: U002 + je 10 pg

2: AE F075736

3: AE F115008
Quantify Sample Report

Sample List: C:\Data\AE F075032\CR99032.PRO\SampleDB\sch003
Last modified: Thu Dec 09 13:31:50 1999
Method: C:\data\AE F075032\CR99032.PRO\MethodDB\EM F13990
Last modified: Fri Nov 12 07:28:31 1999
Job Code:

Printed: Fri Dec 10 07:33:06 1999

Name: R032
Text: Kontr. ESP0001 1N1Aa + je 0.02 ug / kg

2: AE F075736

AgrEvo RCS LC/MS-MS1 09-Dec-1999 20:14:36
Kontr. ESP0001 1N1Aa + je 0.02 ug / kg
R032 Sm (Mn, 2x3)

MRM of 5 Channels ES+
382.20 > 167.00
1.88e3
Area

18.88
465

# RT Flags  Area Mod. User Mod. Time Mod. Date
2 16.881 bb  465
3 18.836 bb  260

3: AE F115008

AgrEvo RCS LC/MS-MS1 09-Dec-1999 20:14:36
Kontr. ESP0001 1N1Aa + je 0.02 ug / kg
R032 Sm (Mn, 2x3)

MRM of 5 Channels ES+
508.20 > 167.00
1.13e3
Area

18.86
260
Quantify Sample Report
Page 13

Sample List: C:\data\AE F075032\CR99032.PRO\SampleDB\sch001
Last modified: Fri Dec 03 08:58:09 1999
Method: C:\data\AE F075032\CR99032.PRO\MethodDB\EM F13990
Last modified: Fri Nov 12 07:29:31 1999
Job Code:

Printed: Mon Dec 06 07:44:48 1999

Name: R001
Text: Kontr. ESP0001 1N1Aa + je 0.05 ug / kg

2: AE F075736

3: AE F115008
Quantify Sample Report

CR 99/032

Sample List:  C:\data\AE F075032\CR99032.PRO\SampleDB\sch001
Last modified: Fri Dec 03 08:58:09 1999
Method:  C:\data\AE F075032\CR99032.PRO\MethDB\EM F13990
Last modified: Fri Nov 12 07:28:31 1999
Job Code:

Printed:  Mon Dec 06 07:44:48 1999

Name: U001
Text: Kontr. ESP0001 1N1Aa

# RT Flags   Area Mod. User Mod. Time Mod. Date
2   3 18.962 bb 20
Soil type: Loamy sand  
Lab code: I013  
Description: Test  
10 pg /Injection of AE F075736, AE F115008  
Matrix: loamy sand

Quantify Sample Report
CR 99/032

Sample List: C:\Data\AE F075032\CR99032.PRO\SampleDB\sch002
Last modified: Fri Dec 03 14:10:50 1999
Method: C:\data\AE F075032\CR99032.PRO\MethodDB\EM F13990
Last modified: Fri Nov 12 07:28:31 1999
Job Code:

Printed: Mon Dec 06 11:10:47 1999

Name: I013
Text: U003 + je 10 pg

2: AE F075736
AgrEvo RCS LC/MS-MS1  04-Dec-1999
U003 + je 10 pg
I013 Sm (Mn, 2x3)

MRM of 5 Channels ES+
382.20 > 167.00
1.14e3
Area

16.94  277

3: AE F115008
AgrEvo RCS LC/MS-MS1  04-Dec-1999
U003 + je 10 pg
I013 Sm (Mn, 2x3)

MRM of 5 Channels ES+
508.20 > 167.00
1.17e3
Area

18.91  299

#   RT Flags  Area Mod. User Mod. Time Mod. Date
2    16.936 bb  277
3    18.911 bb  299
Soil type: Loamy sand
Lab code: R041
Description: Recovery 0.02 µg/kg of AE F075736, AE F115008
Matrix: loamy sand

Quantify Sample Report
CR99/032

Sample List: C:\Data\AE F075032\CR99032.PRO\SampleDB\sch004
Last modified: Fri Dec 10 08:58:16 1999
Method: C:\data\AE F075032\CR99032.PRO\MethDB\EM F13990
Last modified: Fri Nov 12 07:28:31 1999
Job Code:

Printed: Mon Dec 13 07:22:53 1999

Name: R041
Text: Kontr. ITA0001 1N1Aa + je 0.02 ug / kg

2: AE F075736
AgrEvo RCS LC/MS-MS1 10-Dec-1999 10:58:58 Schuld
Kontr. ITA0001 1N1Aa + je 0.02 ug / kg
R041 Sm (Mn, 2x3)

16.90
493

3: AE F115008
AgrEvo RCS LC/MS-MS1 10-Dec-1999 10:58:58 Schuld
Kontr. ITA0001 1N1Aa + je 0.02 ug / kg
R041 Sm (Mn, 2x3)

18.88
371

# RT Flags Area Mod. User Mod. Time Mod. Date
2 16.900 bb 493
3 18.876 bb 371
Quantify Sample Report

CR 99/032

Sample List: C:\Data\AE F075032\CR99032.PRO\SampleDB\sch002
Last modified: Fri Dec 03 14:10:50 1999
Method: C:\data\AE F075032\CR99032.PRO\MethodDB\EM F13990
Last modified: Fri Nov 12 07:28:31 1999
Job Code:

Printed: Mon Dec 06 11:10:47 1999

Name: R017
xt: Kontr. ITA0001 1N1Aa + je 0.05 ug / kg

2: AE F075736

AgrEvo RCS LC/MS-MS1 04-Dec-1999 06:46:48
Kontr. ITA0001 1N1Aa + je 0.05 ug / kg
R017 Sm (Mn, 2x3)

MRM of 5 Channels ES+
382.20 > 167.00
1.83e3
Area

3: AE F115008

AgrEvo RCS LC/MS-MS1 04-Dec-1999 06:46:48
Kontr. ITA0001 1N1Aa + je 0.05 ug / kg
R017 Sm (Mn, 2x3)

MRM of 5 Channels ES+
508.20 > 167.00
1.40e3
Area