

EURL-SRM - Analytical Observations Report

concerning the following...

- **Compound(s):** Sulfuryl fluoride
- **Commodities:** cereals, nuts, pulses and other dry materials
- **Extraction Method(s):** none
- **Instrumental analysis:** Headspace-GC/MS

Analysis of the Fumigant Sulfuryl Fluoride Applying Headspace-GC-MSD

Version 1 (last update: March 2018)

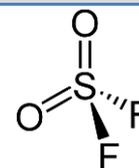
Background information / Initial Observations:

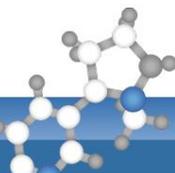
Sulfuryl fluoride was introduced in the 1950s as a fumigant for the control of insect pests in wood especially termites. It has also been used to control rodents. Following the Montreal agreement and the resulting decrease in the use of methyl bromide sulfuryl fluoride has become more important substitute. Sulfuryl fluoride is furthermore considered as an alternative to phosphine, which is more critical in terms of acute toxicity. It is mainly used to fumigate buildings, shipping containers, ships and wood products.

Food applications of sulfuryl fluoride include the fumigation of dried fruit, tree nuts, dry pulses as well as cereals. It is also used to treat empty storage rooms, silos and grain processing facilities. In the EU residues resulting from applications of sulfuryl fluoride are regulated either via an MRL for sulfuryl fluoride as well as via an MRL for fluoride, which is formed when sulfuryl fluoride decomposes. Fluoride is thought to be the actual active component as it inhibits the breakdown of fatty acids within the target organisms.

Compound details:

Sulfuryl Fluoride (CAS: 2699-79-8), IUPAC name: sulfuryl fluoride	
Parameter	Value
Molecular Mass	102.06 g/mol
Exact mass	101.958708 Da
Form	Colorless, odorless gas
Solubility	1.04 g/L (at 20°C) in water 71 g/L in acetone
LogP	0.14 (at 20°C)
Hydrolysis (DT50)	6.7 h (pH 7), 4.0 min (pH 9); @ 20 °C
Boiling point	-54°C
Vapor pressure	1.61 10 ⁶ Pa (20°C)
Residue definition EU	1) <u>Sulfuryl fluoride</u> : MRLs, e.g. 10 mg/kg in tree nuts, 0.05 mg/kg in herbal infusions, MRL*s = 0.01mg/kg in most commodities and 0.02 in teas, coffee etc. 2) <u>Fluoride ion</u> : MRLs, e.g. 350 mg/kg in teas, 25 mg/kg in tree nuts, 10 mg/kg in herbal infusions and hops as well as 5 mg/kg in coffee beans and spices, MRL* = 2 mg/kg for all commodities of plant origin
Sulfuryl fluoride is approved in...	BE, DE, ES, FR, IE, IT, NL, PT, UK
ADI	0.014 mg/kg bw per day (Reg. (EU) 2017/270) / 0.7 mg/kg bw (Reg. (EU) 2017/270)
ARfD	0.01 mg/kg bw per day / 0.3 mg/kg bw (JMPR 2005)





Chemicals¹:

Substance	Purity	CAS	Source
Sulfuryl fluoride in N ₂ 100 ppm	>99.9%	2699-79-8	Linde AG München, Germany
Sulfuryl fluoride in N ₂ 10 ppm	>99.9%	2699-79-8	Linde AG München, Germany
Sulfuric acid (concentrated) Aqueous solutions thereof 5% (v/v) and 10% (v/v) are prepared	analysis grade		Merck, Darmstadt, Germany

Apparatus

Grindomix GM 200 knife mill (Retsch Haan, Germany)

Tedlar gas sampling bags (Nr. 24633 Supelco #, Germany)

gas tight syringes (PN 1710 100 µL and PN 1001 1000 µL from Hamilton #, Germany)

analytical balances capable of weighing to 0.1 mg or to 0.01 g (Mettler-Toledo Greifensee, Switzerland).

GC-MSD: Agilent 6890 GC coupled to 5973 MSD (Waldbronn, Germany) manually tuned to achieve high sensitivity in the low mass area,

Autosampler: MPS2 sampler (Gerstel Mülheim/Ruhr, Germany) with a head space agitator unit and a 2.5 mL syringe

Injection system: KAS 4 PTV with a cryo system at -80°C (liquid nitrogen)

Liners: filled with Tenax (Gerstel Mülheim/Ruhr, Germany).

Column: Rt-Q-Bond PLOT column (30 m × 0.32 mm × 10 µm) (Restek Bad Homburg, Germany) connected to a restriction capillary (5 m × 0.25 mm) (Agilent Waldbronn, Germany), to prevent single loose particles of the stationary phase from entering the ion source of the MSD

Sample Preparation

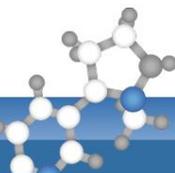
Cereals, pulses or tree nuts are ground with a knife mill.

Granular samples: 3g of **granular samples** (e.g. whole or coarsely milled grains) are weighed in a headspace vial and sulfuric acid 5 % is speedily added up to a level of 15 mL into the vial.

Powdery samples: 1 g of the powdery sample is weighed into a head space vial and 7 mL of water are added. Then the vial is closed with a rubber plug and vigorously shaken to ensure that the material is entirely wetted. Subsequently, the vial is opened again, quickly filled up to a 15 mL level with sulfuric acid 10 % by pouring from a small beaker and immediately closed again with a screw cap.

In case of a standard addition approach make sure to weigh the same amount of sample in each vial and to add the same amount of sulfuric acid (e.g. 10 mL or 12 mL). In this case there is no need to fill-up the vial to a pre-defined level.

¹ **Disclaimer:** Names of companies are given for the convenience of the reader and do not indicate any preference by the EURL-SRM towards these companies and their products



Headspace GC-MS analysis

Table 1: Instrumentation details

Headspace conditions	
Agitator temperature	80°C
Incubation time	10 min
Shaking speed	500 rotations per min
Shaking interval	5 s followed by a 2 s break
Syringe temperature	85°C
Injection volume	2000 µL
Draw speed	200 µL/s
Injection speed	500 µL/s
PTV conditions	
Initial temperature	-110°C with 0.1. min initial time
Heating ramp	150°C with a rate of 12°C/min
Hold time	2 min
Oven	
Carrier gas flow (Hydrogen)	2.2 mL/min (constant flow mode)
Split ratio	5:1
Oven temperature	35°C for 3 min
Heating ramps	10°C/min to 100°C, then 35°C/min to 200°C
Final time	4 min
Total run time	16.4 min
MSD	
Transfer line temperature	240°C
Solvent delay	4 min
SIM mode recording	m/z 83
Dwell time	100 ms for each ion
Tune mode	Manual tune for very low masses

Experiments conducted and observations:

The first experiments were performed applying the previously developed headspace GC-MS method for phosphine². Sulfurylfluorid has a boiling point of -55°C and a lower vapor pressure than phosphine with a boiling point of -87.7°C. The compound should, therefore, in theory, be easier to trap. Unfortunately, however, when using the instrument settings for phosphine the peak shape became very poor with a clearly visible fronting (see figure 1). This behavior may be related to a better affinity of phosphine towards the Tenax sorbent material within the liner.

To achieve a better chromatographic peak, several parameters were varied. Finally a reduction of the trap temperature to -110°C was necessary to obtain a well-defined peak.

² http://ejournal.cvuas.de/docs/cvuas_ejournal_201402.pdf

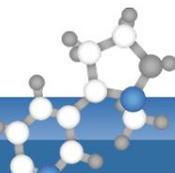
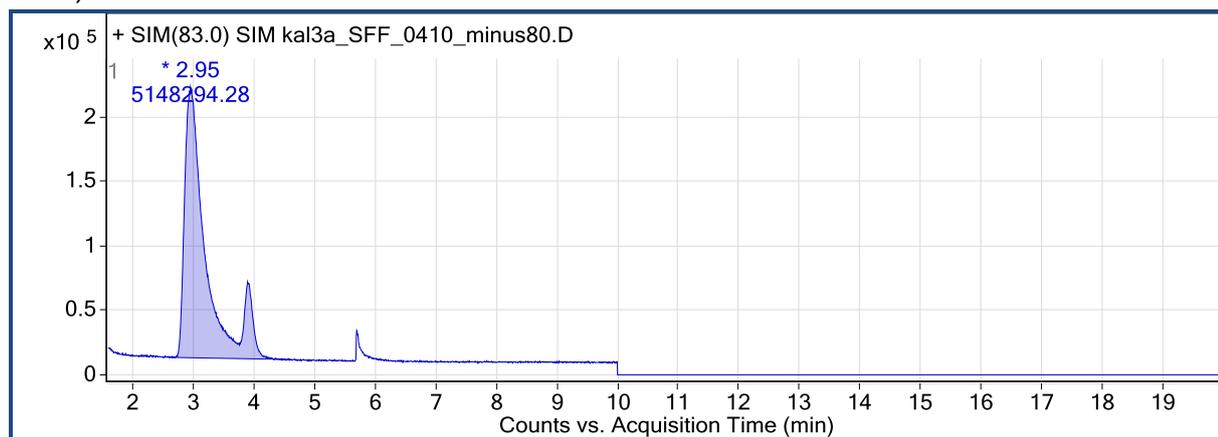
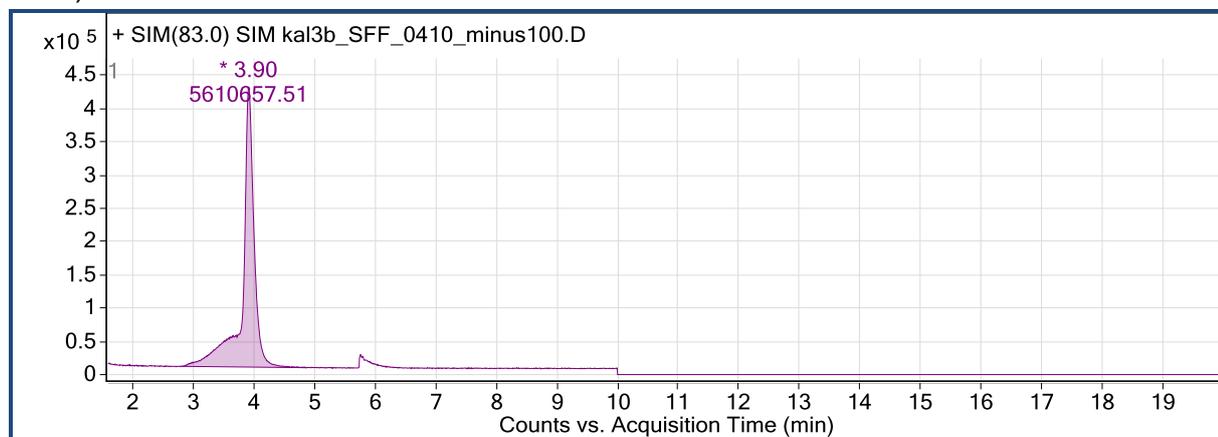


Figure 1: Peak shape of Sulfuryl fluoride at varying trapping temperature -80°C , -100°C and -110°C , injection volume $2000\ \mu\text{L}$

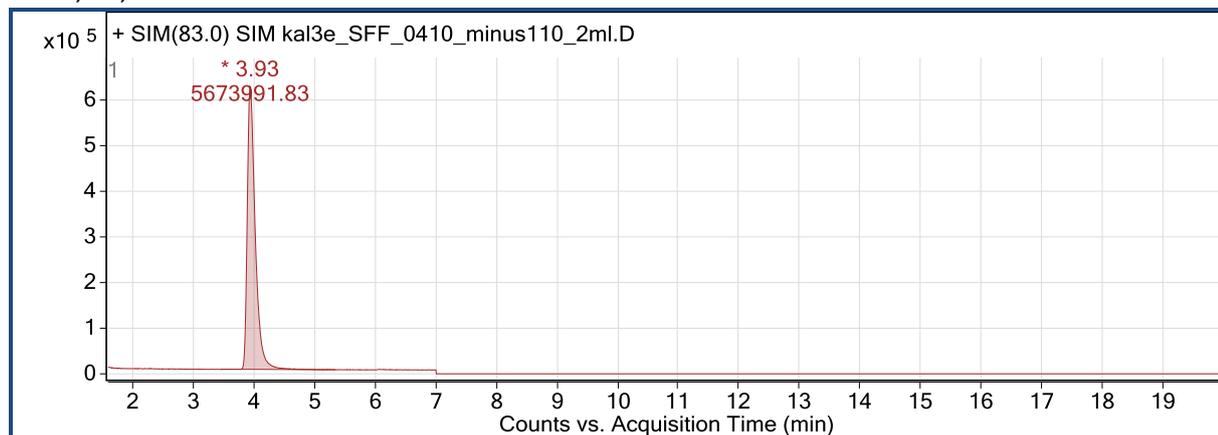
a) -80°C

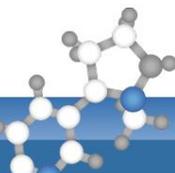


b) -100°C



a) c) -110°C





Calibration:

Calibrations are linear up to 50 µg/kg at least. As matrix-effects may occur matrix-matched calibration or preferably calibration via standard additions is recommended.

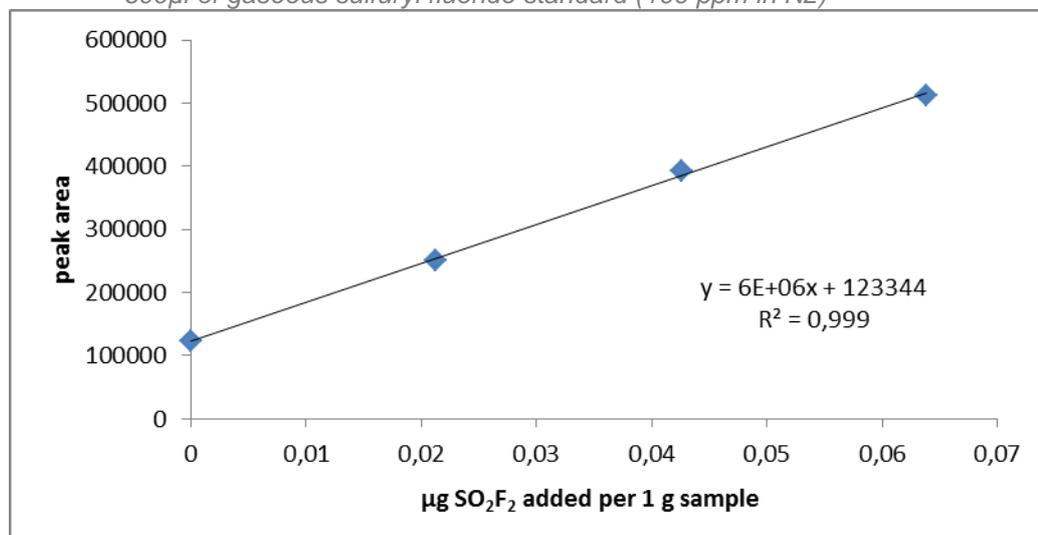
The sensitivity of the method is very good and the MRL* of 0.01 mg/kg can thus be easily monitored using this method.

Exemplary validation experiment:

To validate the method a calibration curve was conducted by injecting the same matrix 4 times but spiked with increasing amounts of sulfuryl fluoride. Considering the lowest spiking level (corresponding to 0.021 mg/kg) as the “unknown” level to be quantified, the calculated recovery rate was 94%.

The different pressure increase caused by the addition of different volume of gaseous sulfuryl fluoride standard did not seem to have any major impact on the linearity of the method and was not taken into account.

Figure 3: Standard addition of SO₂F₂ to soy flour containing 0,021 mg/kg, portion size 1 g, injection volume 1 mL, and spiking volume was 150µl = “unknown”, 300µl, 450µl and 600µl of gaseous sulfuryl fluoride standard (100 ppm in N₂)



Discussion and conclusions:

A method was developed allowing the sensitive and accurate analysis of sulfuryl fluoride residues in dry food commodities.

History

Action	When	Document Version
Observation document placed on-line	April 2018	V1