



Open Archive Toulouse Archive Ouverte

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is an author's version published in: <http://oatao.univ-toulouse.fr/24301>

Official URL: <https://doi.org/10.1080/03067319.2019.1650919>

To cite this version:

Vitola Pasetto, Leticia^{ORCID} and Richard, Romain^{ORCID} and Pic, Jean-Stéphane and Manero, Marie-Hélène^{ORCID} and Violleau, Frédéric^{ORCID} and Simon, Valérie^{ORCID}
Hydrogen sulphide quantification by SIFT/MS: highlighting the influence of gas moisture. (2019) International Journal of Environmental Analytical Chemistry. ISSN 0306-7319

Any correspondence concerning this service should be sent to the repository administrator: tech-oatao@listes-diff.inp-toulouse.fr

Hydrogen sulphide quantification by SIFT/MS: highlighting the influence of gas moisture

Leticia Vitola Pasetto^{a,b}, Romain Richard ^a, Jean-Stéphane Pic^c, Marie-Hélène Manero ^a, Frédéric Violleau ^b and Valérie Simon ^b

^aLaboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France; ^bLaboratoire de Chimie Agro-industrielle, LCA, Université de Toulouse, INRA, INPT, Toulouse, France; ^cToulouse Biotechnology Institute, Bio & Chemical Engineering, TBI, Université de Toulouse, CNRS, INRA, INSA, Toulouse, France

ABSTRACT

The quantification of hydrogen sulphide (H₂S) by Selected Ion Flow Tube coupled with Mass Spectrometry (SIFT/MS) was investigated for application in industrial emission context, usually faced with concentrations of water vapour higher than the saturation at room condition. H₂S concentrations measured by SIFT/MS (using nitrogen as carrier gas and flow tube temperature at 119°C) were affected by water content, reducing the sensibility for H₂S measurements. Accurate concentrations were obtained when the influence of water was considered on SIFT/MS analysis, requiring although the information about water content in the sample. In addition, the association of low concentration of H₂S (around 50 ppbv) and high humidity level (4.0 %vol of water) was highlighted as a critical point for measuring H₂S by SIFT/MS, due to the sensibility reduction as function of water content and the measurement uncertainty enhancement at low signal intensity.

KEYWORDS

Chemical ionisation mass spectrometry; hydrogen sulphide; water interference; selected ion flow tube mass spectrometry

1. Introduction

Reduced sulphur compounds (RSCs) are key-compounds in Environmental Chemistry due to their association to acid rain, odour nuisance and potential health hazard [1–3]. They are emitted from natural and industrial activities, such as volcanic eruptions, landfills, wastewater treatments, pulp-and-paper and chemical plants [4,5]. Allowing its low odour threshold limit (0.15 ppbv [6]) to its common detection in polluted atmospheric analysis [4,7], hydrogen sulphide (H₂S) was chosen as a model compound for RSCs. Furthermore, H₂S is the major impurity in the natural gas, which concentration must be monitored to ensure the regulatory level [8,9].

Several analytical methods have been developed to quantify H₂S. Those based on Gas Chromatography (GC) are the most used techniques, in combination with specific sulphur detectors such as Electron Capture Detector (ECD), Flame Photometric Detector (FPD), Pulsed Flame Photometric Detector (PFPD), Sulphur Chemiluminescence Detector (SCD) and Atomic Emission Detection (AED) [2,3]. The analysis of H₂S based on GC usually applies

a Thermodesorption (TD) device to obtain lower limit of detection (LOD). Even if interesting LOD values could be achieved by GC methods, chromatographic and sampling interferences can still occur in presence of water and oxidants (such as ozone, sulphur dioxide and nitrogen oxides) [2,4].

More recently and in parallel to GC-based methods, the use of Chemical Ionization coupled with Mass Spectrometry (ICMS) has been reported in literature for H₂S quantification [9–12]. Real-time analysis, high sensitivity and low LOD are some of the advantages common to ICMS techniques, such as Proton Transfer Reaction Mass Spectrometry (PTR/MS) and Selected Ion Flow Tube Mass Spectrometry (SIFT/MS). For both PTR/MS and SIFT/MS, H₂S concentration is calculated based on the ionisation reaction of H₂S with H₃O⁺ precursor ion, which generates the H₃S⁺ product ion, since the proton affinity of H₂S (705 kJ mol⁻¹) is higher than H₂O (691 kJ mol⁻¹) [9,10,12]. However, this slight difference on proton affinity values may lead to a more complex analysis of H₂S than usual.

Previously studies regarding the quantification of H₂S in humid air by PTR/MS [9,12] have demonstrated that, in presence of water, the reverse ionisation reaction (proton transfer from H₃S⁺ to H₂O) occurs and H₂S concentrations must be corrected regarding the water content. In addition, it was reported a decrease on the sensitivity of PTR/MS when analysing H₂S in presence of water [9]. Similar disturbance on H₂S measurements due to humidity presence was also observed in SIFT/MS analysis [10] and thus, accurate H₂S concentrations are only possible if the secondary reactions of H₃S⁺ are considered. Furthermore, the water clusters formation of H₃S⁺.H₂O and H₃O⁺.(H₂O)_{n=1,2,3} (hydrated hydronium ions) must be taking into account [10]. In addition to the proton transfer from H₃S⁺ to H₂O, Spanel and Smith [10] have indicated the exothermic switching reaction of H₃S⁺.(H₂O)_{n=1,2} with H₂O (generating H₃O⁺.(H₂O)_{n=1,2} and H₂S) may also occur. According to another study from Spanel and Smith [13], the clusters formation happens *via* sequential three-body association, in which helium molecule (carrier/inert gas) present at the reaction chamber (flow tube) acts as stabilising-agent. Therefore, as H₂S quantification depends on the water clusters generation, which in turn is influenced by the inert compound, the use of a different molecule as carrier gas could lead to distinct results in terms of H₂S quantification in humid air.

In this work, the influence of humidity in the quantification of H₂S by SIFT/MS was deeper investigated to adequate SIFT/MS analysis for industrial emission context (usually faced with humidity content higher than atmospheric level [14–16]). The impact of the humidity on H₂S quantification was investigated by monitoring the sensibility and the uncertainty of SIFT/MS device (which was operated in different conditions compared to those reported in the literature [10], *i.e.* higher flow tube temperature and nitrogen as carrier gas). In addition, an empirical model was proposed to satisfactorily quantify H₂S concentrations even in extreme humidity conditions.

2. Experimental

2.1. Materials

The H₂S calibration was performed between 0.05 and 1.6 ppmv (in 6 levels) from the mix of a gas cylinder standard (100 ppmv of H₂S in nitrogen, Air Liquide, France) and an air stream (ZR55, oil-free air ISO 8573–1 class 0, Atlas Copco France) integrated to air filter

(Olympian Plus, Norgren, UK), which gas flows were controlled by mass flowmeters (SLA 5850S-B Brooks Instruments, USA). A humidification system (Serv'Instrumentation, France) was employed to generate calibrated water content ($[H_2O]$) from 0.01%vol (dry air, dew point equal to -40°C at 101.3 kPa) until 5.00%vol (dew point equal to 33°C at 101.3 kPa), in 7 levels, which are described in Table 1. When water concentration reaches 2.00%vol (equivalent to dew point of 17°C), the air stream is nearly saturated ($> 80\%$ of relative humidity) at room conditions (20°C and 101.3 kPa). Therefore, for the conditions when water content was superior to 2.00%vol, the system was heated until 40°C thanks to a hot circulating oil bath (Model 1160S, VWR, USA), composed of a stainless steel smooth-coil immersed in a synthetic thermoliquid (Ultra 350, Lauda, Germany) installed at the air line after the humidification system. The gas line between the mixture point and the SIFT/MS was isolated and heated using a heated cable (FGR-100, Omegalux, France) to prevent condensation.

2.2. SIFT-MS analysis

In SIFT/MS system, H_2S concentration is determined thanks to the reaction of the molecule with the H_3O^+ precursor ion and the detection of its product ion by MS. Produced by a microwave discharge in SIFT/MS device (Voice 200*ultra*, Syft Technologies Ltd, New Zealand), the precursor ion was selected by a first quadrupole mass filter and injected to the flow tube by a nitrogen flow (180 NmL min^{-1}) as carrier gas, whereas the sample was introduced by a calibrated capillary (20 NmL min^{-1}). In the flow tube (kept at 119°C and 0.07 kPa), the reaction between the analyte (neutral compound) and the selected precursor ion was held, generating product ions with specific mass-to-charge ratios (m/z). The product ions were quantified by a second quadrupole mass spectrometer, calculating a count rate (signal intensity in counts s^{-1}) [17–19].

The analyte present in the sample ($[A]_{\text{sample}}$) was diluted by the carrier gas in the flow tube, whose analyte concentration ($[A]_{\text{ft}}$) depends on the operating conditions of the flow tube – temperature (T_{ft}), pressure (P_{ft}), sample flow (φ_s), carrier gas flow (φ_c) – and on the Boltzmann constant (k_b), as described by Equation (1) [17].

$$[A]_{\text{ft}} = [A]_{\text{sample}} \frac{P_{\text{ft}}}{T_{\text{ft}} k_b} \frac{\varphi_s}{(\varphi_s + \varphi_c)} \quad (1)$$

$[A]_{\text{ft}}$ was also calculated by Equation (2) based on the rate coefficient (k) of the reaction between the neutral compound and the precursor ion, the reaction time in the flow tube (t), the ratio between the precursor ion count rate at time equal to 0 ($[I_0]$) and time t ($[I]$) [17,20]. For the Syft model used for this project, reaction time was around 5 ms.

Table 1. Levels of humidity in the air sample studied at atmospheric pressure.

$[H_2O]$ (%vol)	Dew point ($^\circ\text{C}$)	Air temperature ($^\circ\text{C}$)	Relative humidity (%)
0.01	-40	20	0
0.50	-3.5	20	20
1.20	9.5	20	50
2.00	17	20	75
2.30	20	40	35
3.50	26	40	50
5.00	33	40	70

$$\frac{[I]}{[I]_0} = \exp(-k[A]_{ft}t) \quad (2)$$

As the product ion count rate ($[P]$) can be expressed as the difference between $[I]_0$ and $[I]$ (in case of mono-component and m/z inferior to 100 [21]), Equation (2) becomes Equation (3).

$$\frac{[P]}{[I]} = \frac{1 - \exp(-k[A]_{ft}t)}{\exp(-k[A]_{ft}t)} \quad (3)$$

At low analyte concentrations, Equation (3) can be approximated to a linear correlation between $[A]_{ft}$ and $[P]/[I]$ ratio (Equation 4), if the limit of $k[A]_{ft}t$ approaching zero is considered in the exponential expression [17]. This linear approximation is only valid for small values of $[P]/[I]$ ($\ll 1$). Moreover, Equation (4) also integrates the diffusion-correcting factor (D_f), which is usually assumed as unity except when the size of the precursor and the product ion is greatly different [17,21]. In presence of water, clusters ions are likely generated and therefore, the count rates of all product ions originated from analyte A, and all secondary clusters precursor ions with its respective rate coefficient must be taking into account to correctly calculate $[A]_{ft}$ [17].

$$[A]_{ft} = \frac{D_f \sum_{i=1}^n [P_i]}{t \sum_{j=1}^m [I_j] k_j} \quad (4)$$

In case of H_2S , rate coefficients proposed in the kinetic library from LabSyft® 1.6.2 (analytical software related to SIFT/MS instrument, Syft Technologies Ltd, New Zealand) are shown in Table 2 for helium as carrier gas. These values are in agreement with several studies in the literature [10,11,22]. Two product ions are proposed: H_3S^+ with m/z ratio equal to 35 and $H_3S^+ \cdot (H_2O)$ with m/z equal to 53.

According to studies carried out by Milligan et al. [23], in SIFT/MS instrument, LOD is calculated considering the confidence level equal to three standard deviations above background, whereas limit of quantification (LOQ) is the lowest concentration that can be measured with a precision of $\pm 20\%$ [18,23]. These concentrations are obtained by Equation (5) (LOD) and Equation (6) (LOQ), where b_μ represents the mean background count rate (counts s^{-1}) of the product ion at specific m/z ratio, t_m the measurement time (s) and s the sensitivity (counts s^{-1} ppbv $^{-1}$). In this study, b_μ and t_m were calculated from a blank analysis, *i.e.* without the presence of the analyte (H_2S), but still injecting air at its respective humidity content in the SIFT/MS instrument (b_μ represents the global blank, whose noise value was related to the experimental set-up and the SIFT/MS device). Sensitivity was defined as the number of product ions (counts s^{-1}) at the specific m/z ratio produced for a given concentration of analyte [24,25]. It is important to highlight

Table 2. Rate coefficients of H_2S .

Precursor ion	Rate coefficient (cm ³ molecule ⁻¹ s ⁻¹)
H_3O^+ (m/z 19)	1.6×10^{-9}
$H_3O^+ \cdot (H_2O)$ (m/z 37)	5×10^{-12}
$H_3O^+ \cdot (H_2O)_2$ (m/z 55)	5×10^{-12}
$H_3O^+ \cdot (H_2O)_3$ (m/z 73)	5×10^{-12}

that, in SIFT/MS analysis, the measurement time affects the LOD and LOQ values (the longer the measurement, the lower LOD and LOQ).

$$\text{LOD}_{\text{ppbv}} = \frac{3\sqrt{b_{\mu}t_m}}{s t_m} \quad (5)$$

$$\text{LOQ}_{\text{ppbv}} = \frac{25 + 5\sqrt{25 + 4 b_{\mu}t_m}}{2 s t_m} \quad (6)$$

3. Results and discussion

3.1. Accurate H₂S concentration in presence of water

Even applying different operating conditions on SIFT/MS device (flow tube temperature at 119°C and nitrogen as carrier gas), the injection of a humid air has greatly promoted the water clusters formation, as it has been reported in the literature for helium and flow tube temperature at 25°C [10,13]. Increasing the water concentration in the flow tube (calculated by Equation 1 and only considering the water amount injected by the sample), the signal intensity of H₃O⁺ (*m/z* 19) precursor ion has progressively decreased, whereas H₃O⁺.(H₂O) (*m/z* 37), H₃O⁺.(H₂O)₂ (*m/z* 55) and H₃O⁺.(H₂O)₃ (*m/z* 73) ions have been more intense, as shown in Figure 1. In dry air condition, the H₃O⁺ (*m/z* 19) precursor ion was the most intense precursor ion. However, when 0.50%vol of H₂O was present in sample air (equivalent to 7×10^{12} molecule cm⁻³ in flow tube), H₃O⁺ (*m/z* 19) intensity was reduced of 60% at a mixing ratio sample-carrier gas equal to 10%. In conditions when more than 0.50%vol of H₂O was present in the sample air, the most intense precursor ions were H₃O⁺.(H₂O) (*m/z* 37) and H₃O⁺.(H₂O)₂ (*m/z* 55). The clusters formation by three-body association with nitrogen molecules may also occur in a sequential mechanism, since the signal intensities of H₃O⁺.(H₂O) (*m/z* 37) and H₃O⁺.(H₂O)₂ (*m/z* 55) did not increase significantly, reaching a plateau for water content higher than 2.00%vol. Meanwhile, H₃O⁺.(H₂O)₃ (*m/z* 73) ion has continued increasing as function of the water concentration.

Even introducing a fixed H₂S concentration in sample air (equal to 0.5 ppmv), the product ions H₃S⁺ (*m/z* 35) and H₃S⁺.(H₂O) (*m/z* 53) have not resulted in a constant intensity signals, as indicated by Figure 1. Their values have decreased with H₂O concentration increase, in agreement with Spanel and Smith [10], which suggested that reverse ionisation reactions also occur in presence of nitrogen (carrier gas). The decrease of H₃S⁺ (*m/z* 35) with water content seems to be correlated to H₃O⁺ (*m/z* 19) dropping, which could be explained by: (i) the very slow reaction between H₂S and water clusters H₃O⁺.(H₂O) (*m/z* 37), H₃O⁺.(H₂O)₂ (*m/z* 55) and H₃O⁺.(H₂O)₃ (*m/z* 73) (Bohme *et al* [22] and Williams *et al* [11] have reported rate coefficients $<10^{-12}$ cm³ molecule⁻¹ s⁻¹) and (ii) the three-body association reaction of H₃S⁺ and of H₃S⁺.(H₂O) with H₂O molecules and the consequent fast switching reaction of H₃S⁺.(H₂O)_{n=1,2} to H₃O⁺.(H₂O)_{n=1,2} (since the bond between the H₂O molecules are stronger than with H₂S molecules [10]). Yet from Figure 1, H₃S⁺.(H₂O) (*m/z* 53) intensity represented less than 1% of

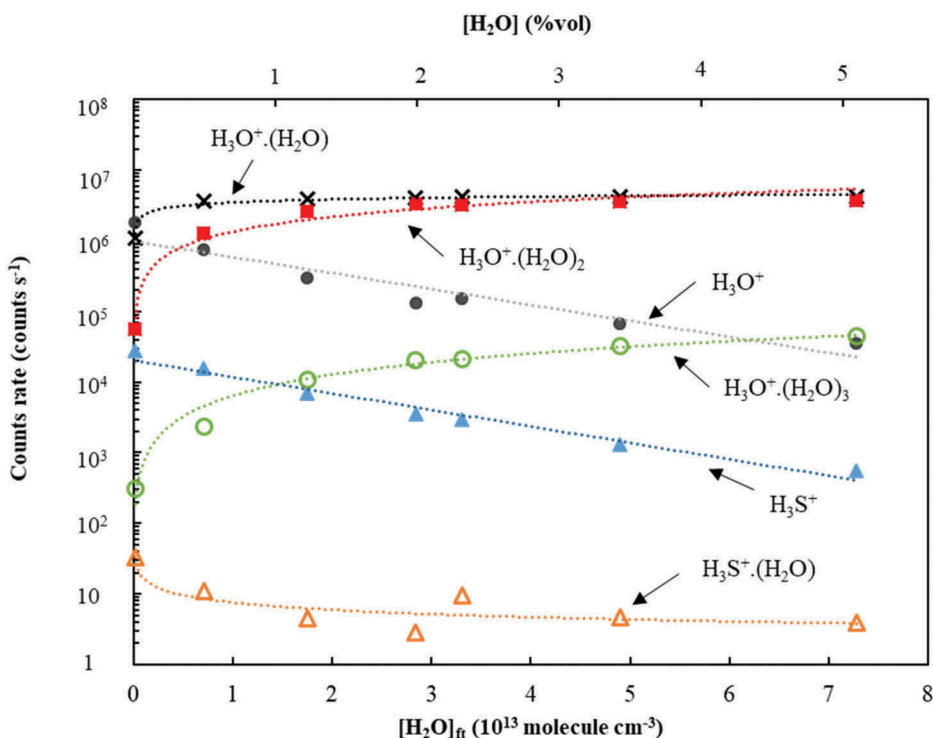


Figure 1. Product and precursor ions counts rate for $[\text{H}_2\text{S}]$ fixed at 0.5 ppmv as function of H_2O content in the sample (in %vol) and its respective H_2O concentration in flow tube after dilution in nitrogen as carrier gas (in molecule cm^{-3} and calculated by Equation 1), without considering the H_2O generated by SIFT/MS ion source. H_3O^+ (m/z 19) (\bullet); $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})$ (m/z 37) (\times); $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2$ (m/z 55) (\blacksquare); $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_3$ (m/z 73) (\circ); H_3S^+ (m/z 35) (\blacktriangle) and $\text{H}_3\text{S}^+\cdot(\text{H}_2\text{O})$ (m/z 53) (\triangle).

H_3S^+ (m/z 35) intensity, which means this product ion can be negligible in Equation (4), without affecting the accurate calculation of H_2S concentration.

These variations on precursor and product ions intensities caused by the water amount were reflected on the calculation of H_2S concentrations. Applying the rate coefficients proposed by LabSyft[®] kinetic library (Table 2), H_2S concentration measured by SIFT/MS showed a deviation compared to standard calibrations (evidenced by the slopes of the linear regression between calibrated and measured concentrations different from 1), except when the dry air was fed (slope of 1.07), as shown in Figure 2(a). In presence of water, the measured H_2S concentrations were falsely high (except for the highest humidity level). The relative gap between the measured and the calibrated H_2S concentrations was enlarged with H_2O concentration until 2.00%vol (slope values equal to 1.34 and 1.67 for respectively 0.50%vol and 2.00%vol of H_2O). However, from 3.50%vol to 5.00%vol, the opposite effect was identified (slope values equal to 1.18 and 0.88 for respectively 3.50%vol and 5.00%vol of H_2O). Spänel and Smith [10] also reported higher measured H_2S concentrations in presence of water (1×10^{13} molecule cm^{-3} in flow tube), which were explained by the large variation of H_3O^+ precursor ions due to clusters formation.

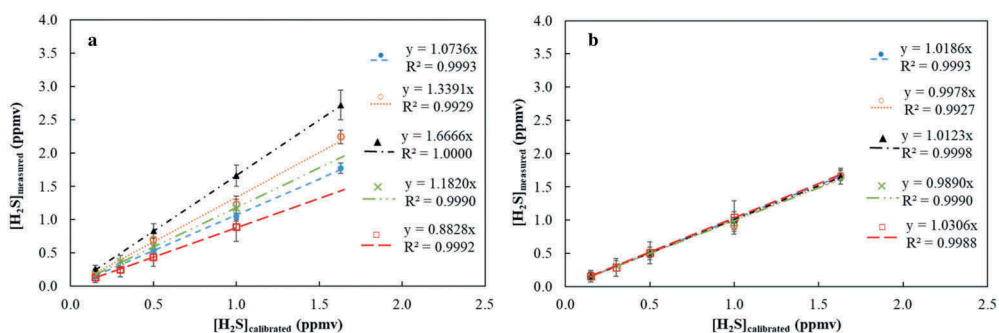


Figure 2. Comparison between measured and calibrated H_2S concentrations for 5 humidity levels and its respective linear regression (dotted lines): 0.01%vol of H_2O (●); 0.50%vol of H_2O (○); 2.00% vol of H_2O (▲); 3.50%vol of H_2O (✕) and 5.00%vol of H_2O (□). (a) Considering the ionisation rate coefficients values shown in Table 2. (b) Considering the apparent product formation rate after correcting according to water amount.

Therefore, it is possible to conclude that the rate coefficients values used by LabSyft[®] kinetic library did not satisfactorily describe the ionisation reaction of H_2S by H_3O^+ precursor ion in presence of water when applying flow tube temperature at 119°C and nitrogen as carrier gas. Applying a similar methodology proposed to measurements of H_2S using PTR/MS [9,12], the rate coefficient of H_3O^+ (m/z 19) was corrected integrating the water concentration and neglecting all reactions of H_2S with water clusters $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ (m/z 37), $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$ (m/z 55) and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ (m/z 73). Therefore, these water clusters ions were no more considered as precursor ions in LabSyft[®] software. The apparent product formation rate (kap_{19}) for the H_3O^+ (m/z 19) precursor ion was calculated multiplying the rate coefficient of H_3O^+ (m/z 19) at dry air ($1.6 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) by the ratio of the H_2S concentration measured by SIFT/MS (with only H_3O^+ as precursor ion and rate coefficient of dry air) and the calibrated H_2S concentration. The calculation of kap_{19} was carried out for all levels of H_2S and H_2O concentrations and their values are presented in Figure 3 with their respective uncertainties. These ones were calculated by propagation error method, which includes the standard deviation of kap_{19} calculated for each H_2S concentration level and the uncertainty from the experimental dispositive to generate the diluted gas mixture (estimated as 10% to lowest H_2S concentrations). In agreement with Li *et al* results [9], the apparent rate coefficient has shown an exponential relationship with humidity level. The value of kap_{19} largely depends on the humidity level, dropping by about a factor of 100 in condition with high water amount (5.00%vol). The increase of the H_2O concentration probably enhances the reverse ionisation reaction (from H_3S^+ to H_2O), reducing, therefore, the apparent rate coefficient of the reaction between H_2S with H_3O^+ .

The H_2S concentrations determined from the corrected values of rate coefficients of precursor ion H_3O^+ (m/z 19) for each level of H_2O concentration are shown in Figure 2(b), which are in excellent accord with the calibrated H_2S concentrations (all slopes are close to 1 with excellent correlation coefficients). However, the major drawback of this correction method by kap_{19} is that accurate quantification of H_2S by SIFT/MS is only possible if the humidity level of sample is known. Meanwhile, at a fixed level of humidity, the

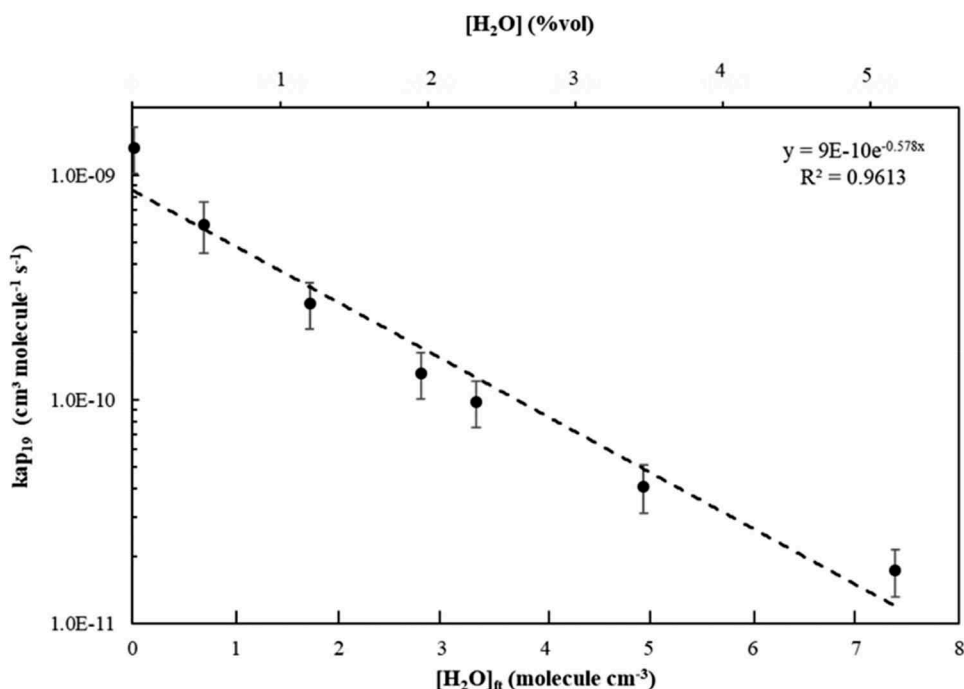


Figure 3. Apparent product formation rate of precursor ion H_3O^+ (m/z 19) (kap_{19}) as function of H_2O concentration.

H_2S concentration followed a linear correlation (R^2 close to 1), which means that even if the absolute value of H_2S is not accurate, H_2S concentrations is always proportional to the signal intensity of H_3S^+ (m/z 35) product ion (for the concentration range studied in this work).

3.2. Analytical performance

The H_2O concentration has also shown a serious impact on SIFT/MS sensitivity for H_2S , as shown in Figure 4(b). In dry sample conditions and for a sample flow equal to 20 NmL min^{-1} , each ppmv of H_2S generated around 60 000 counts s^{-1} at H_3S^+ (m/z 35). However, when 1.00%vol of H_2O were present in sample gas, H_3S^+ (m/z 35) intensity dropped to 15 000 counts s^{-1} for each ppmv of H_2S injected in the sample. This reduction of the sensitivity of SIFT/MS could also be observed in Figure 1: at a fixed H_2S concentration, H_3S^+ (m/z 35) product ion gradually decreased with the humidity level augmentation.

The sensitivity-reducing phenomena with humidity caused two main consequences on analytical performance of SIFT/MS: (i) the increasing of LOD and LOQ and (ii) the raise of uncertainty for H_2S measurements. LOD and LOQ were calculated for five different levels of humidity and considering a measurement time of 100 s (Table 3). Comparing, for example, LOQ at dry condition to 4.00%vol of H_2O , the strong effect of water interference is clearly observed: LOQ has increased from 0.040 ± 0.008 ppbv to 1.4 ± 0.3 ppbv. Although, even in critical humidity conditions, LOD of SIFT/MS for

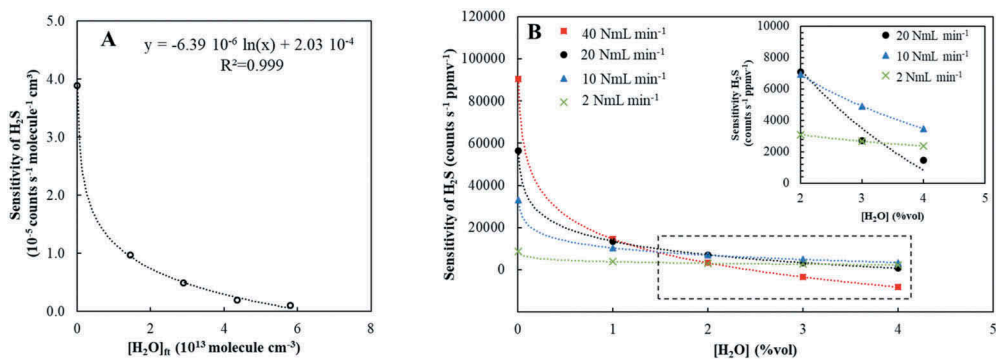


Figure 4. The sensitivity of SIFT/MS for H₂S quantification as function of humidity level. (a) Experimental values obtained with $\varphi_s = 20 \text{ NmL min}^{-1}$ and considering the sensitivity of H₂S and the H₂O content in the flow tube. (b) Effect of sample flow on the sensitivity for 4 sample flows: $\varphi_s = 40 \text{ NmL min}^{-1}$ (■), $\varphi_s = 20 \text{ NmL min}^{-1}$ (●), $\varphi_s = 10 \text{ NmL min}^{-1}$ (▲) and $\varphi_s = 2 \text{ NmL min}^{-1}$ (✕).

Table 3. LOD and LOQ of SIFT/MS for H₂S (considering a measurement time of 100 s).

[H ₂ O] (%vol)	LOD (ppbv)	LOQ (ppbv)
0.01	0.02	0.04
1.20	0.05	0.1
2.00	0.1	0.2
3.00	0.4	0.7
4.00	0.8	1.4

H₂S measurements has resulted in lower values compared to GC-based methods usually coupled with TD devices: 0.77 ppbv vs 3.8 ppbv [7].

We also observed that, in SIFT/MS, uncertainty of signal intensity is tightly connected to its absolute value, and therefore, the less intense the signal, the bigger the uncertainty. This observation can be exemplified in Figure 5, where four different levels of H₂S concentrations (0.05 ppmv; 0.15 ppmv; 0.5 ppmv and 1 ppmv) are disposed with their respective uncertainties (the standard deviation of a 400 s measurement time analysis measured by SIFT/MS) as function of H₂O concentration. It is clear that the highest uncertainty (around 35%) was obtained at the lowest value of H₂S concentration (0.05 ppmv) coupled with the highest humidity level (4.00%vol of H₂O), whereas at 1.0 ppmv of H₂S and 4.00%vol of H₂O, the relative uncertainty was reduced to 10%. In summary, low concentration of H₂S in combination with high humidity is a critical point for measuring H₂S by SIFT/MS. The augmentation of the relative uncertainty related to the water content becomes less noticeable as the H₂S concentration increases, since the intensity of H₃S⁺ (*m/z* 35) also rises.

The practical uncertainties obtained were greater than the LOQ values, probably because of the uncertainty of the experimental set up to generate the diluted gas mixture. This uncertainty was estimated to 10% for the lowest H₂S concentrations and to 2% for the highest H₂S concentrations.

The negative effect of humidity on the sensitivity of H₂S could be minimise by decreasing the sample flow of the SIFT/MS device, since the lower the quantity of

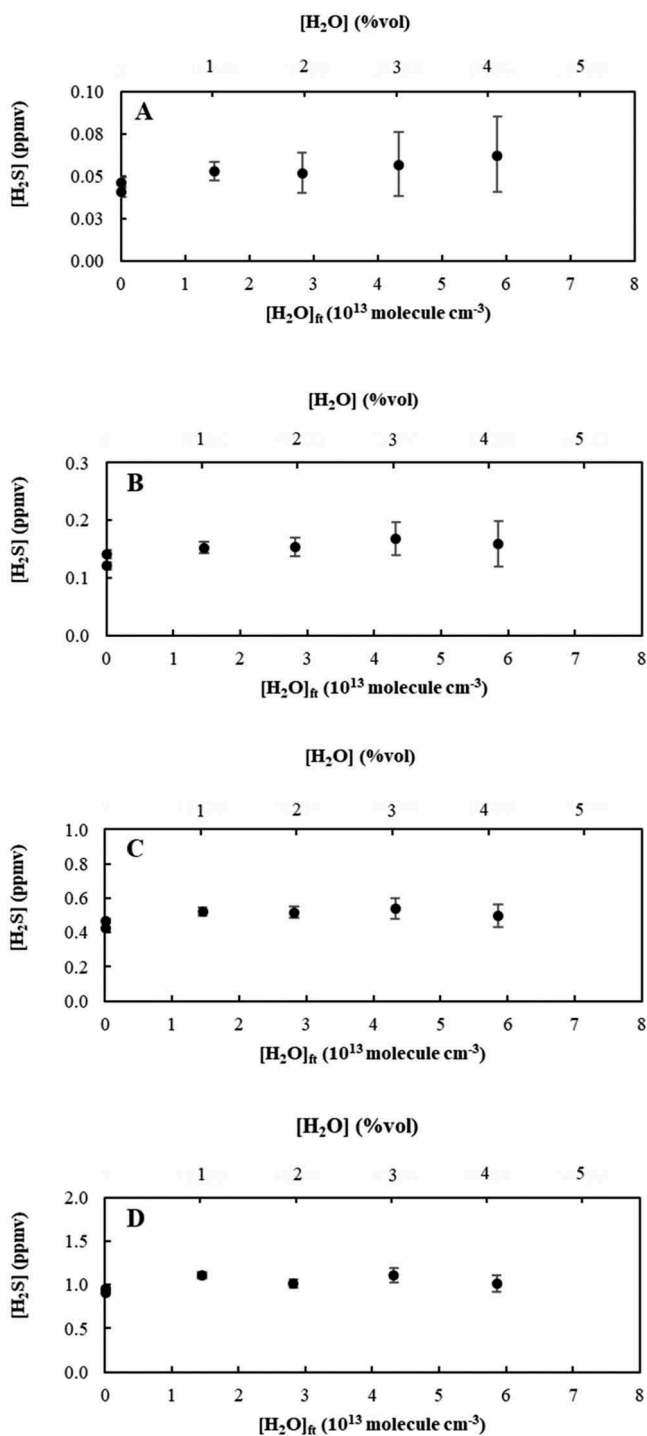


Figure 5. Uncertainty related to H₂O and H₂S levels of concentration. The H₂S concentration axis is limited to the double of the calibrated concentration to express the relative error (calculated as the standard deviation of a 400 s measurement time analysis by SIFT/MS). (a) 0.05 ppmv of H₂S. (b) 0.15 ppmv of H₂S. (c) 0.5 ppmv of H₂S and (d) 1.0 ppmv of H₂S.

water present in the flow tube, the lower the clusters formation. Meanwhile, for a same concentration level in the sample flow, a decrease of the sample flow also reduces the signal intensity of H_3S^+ (m/z 35), which could affect the analysis uncertainty.

In order to consider these two clearly compensating effects and, hence, to obtain an optimum sample flow in extreme air humidity condition, a theoretical study was carried out. We have considered that the sensitivity of H_2S (in counts s^{-1} molecule $^{-1}$ cm^3) – associated to the H_2S concentration in the flow tube – would present the same profile as function of the H_2O concentration in flow tube (in molecule cm^{-3}) regardless of the sample flow. From the experimental values obtained with 20 NmL min^{-1} (the only sample flow experimentally feasible), a natural logarithm expression (R^2 equal to 0.999) was adjusted, correlating the sensitivity of H_2S (in counts s^{-1} molecule $^{-1}$ cm^3) with the $[\text{H}_2\text{O}]_{\text{ft}}$ (in molecule cm^{-3}) as shown in Figure 4(a). Thanks to this expression, we could predict the variation of the sensitivity of H_2S (in counts s^{-1} ppmv $^{-1}$) as a function of H_2O content (in %vol) for three different sample flows (40 NmL min^{-1} , 15 NmL min^{-1} and 2 NmL min^{-1}). These prediction curves are presented in Figure 4(b) simultaneously with the experimental one (20 NmL min^{-1}).

The Figure 4(b) shows that the increase of the sample flow (40 NmL min^{-1}) is disadvantageous for H_2S quantification in extreme humidity conditions (superior to 2.00%vol of H_2O), given that the sensitivity of H_2S decreases vertiginously depending on H_2O concentration. As expected, the decrease of the sample flow (from 20 NmL min^{-1} to 10 NmL min^{-1}) was beneficial since a higher value of sensitivity was obtained for H_2O content superior to 2.00%vol. Nevertheless, when the sample flow was decreased from 10 NmL min^{-1} to 2 NmL min^{-1} , the opposite behaviour was identified: at 4.00%vol of H_2O , the sensitivity at 2 NmL min^{-1} was lower than at 10 NmL min^{-1} , indicating that an optimum value could be calculated. By applying the Generalized Reduced Gradient (GRG) nonlinear method, the optimum sample flow found was 7.3 NmL min^{-1} (obtained considering the highest sensitivity level for $[\text{H}_2\text{O}]$ at 4%vol).

4. Conclusion

The H_2S quantification in real-time analysis can be satisfactorily carried out by SIFT/MS using nitrogen as carrier gas, even in extreme air humidity conditions (from 0.01 to 5.00%vol of H_2O), without requiring any dryer or water trap devices. For that, in order to compensate the water interference, the rate coefficient of the $\text{H}_2\text{S}-\text{H}_3\text{O}^+$ ionisation reaction in SIFT/MS analysis must be corrected regarding the water content and thus, the humidity in the gas matrix must be known.

This study has also evidenced that the use of nitrogen as carrier gas requires precaution regarding the parameters previously obtained using helium. For compounds which clusters formation and/or reverse proton transfer may occur – such as H_2S – complementary studies are necessary for accurate quantification by SIFT/MS.

In addition, we found that (i) the humidity decreased the sensitivity of SIFT/MS for H_2S quantification and (ii) the measurement uncertainty is higher with low signal intensity. Therefore, the association of low H_2S concentration and high humidity is a critical point for H_2S measurements. Uncertainty values around 35% were reported in this critical condition (for the standard sample flow applied in study). A decrease of

the sample flow of SIFT/MS device is suggested if the H₂S quantification has to be carried out in extreme humidity conditions. LOD and LOQ also increased due to the humidity raise, but they were still lower than the values obtained with the traditional analytical method (TD-GC).

Acknowledgments

The authors gratefully acknowledge the financial support for the research by French National Agency for Research and Technology and Agro Innovation International (CIFRE 2015/1233).

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the French National Agency for Research and Technology and Agro Innovation International (CIFRE 2015/1233).

ORCID

Romain Richard  <http://orcid.org/0000-0002-6037-8254>

Marie-Hélène Manero  <http://orcid.org/0000-0002-8598-4250>

Frédéric Violleau  <http://orcid.org/0000-0002-2571-5083>

Valérie Simon  <http://orcid.org/0000-0002-2624-157X>

References

- [1] A.R. Ravishankara, Y. Rudich, R. Talukdar and S.B. Barone, *Philos. Trans. R. Soc. B Biol. Sci.* **352**, 171 (1997). doi:10.1098/rstb.1997.0012.
- [2] S.K. Pandey and K. Kim, *Environ. Sci. Technol.* **43**, 3020 (2009). doi:10.1021/es901110m.
- [3] K.H. Kim, *Environ. Sci. Technol.* **39**, 6765 (2005). doi:10.1021/es050497i.
- [4] E. Borrás, L.A. Tortajada-Genaro and A. Muñoz, *Talanta* **148**, 472 (2016). doi:10.1016/j.talanta.2015.11.021.
- [5] K.C. Li and D. Shooter, *Int. J. Environ. Anal. Chem.* **84**, 749 (2004). doi:10.1080/03067310410001729619.
- [6] E.C. Sivret, B. Wang, G. Parcsi and R.M. Stuetz, *Water Res.* **88**, 308 (2016). doi:10.1016/j.watres.2015.10.020.
- [7] B. Wang, E.C. Sivret, G. Parcsi and R.M. Stuetz, *Talanta* **137**, 71 (2015). doi:10.1016/j.talanta.2014.11.072.
- [8] A.S. Brown, A.M.H. van der Veen, K. Arrhenius, A. Murugan, L.P. Culleton, P.R. Ziel and J. Li, *TrAC - Trends Anal. Chem.* **64**, 42 (2015). doi:10.1016/j.trac.2014.08.012.
- [9] R. Li, C. Warneke, M. Graus, R. Field, F. Geiger, P.R. Veres, J. Soltis, S.M. Li, S.M. Murphy, C. Sweeney, G. Pétron, J.M. Roberts and J. De Gouw, *Atmos. Meas. Tech.* **7**, 3597 (2014). doi:10.5194/amt-7-3597-2014.
- [10] P. Spanel and D. Smith, *Rapid Commun. Mass Spectrom.* **14**, 1136 (2000).
- [11] T.L. Williams, N.G. Adams and L.M. Babcock, *Int. J. Mass Spectrom.* **172**, 149 (1998). doi:10.1016/s0168-1176(97)00081-5.
- [12] A. Feilberg, D. Liu, A.P.S. Adamsen, M.J. Hansen and K.E.N. Jonassen, *Environ. Sci. Technol.* **44**, 5894 (2010). doi:10.1021/es100483s.

- [13] P. Spanel and D. Smith, *Rapid Commun. Mass Spectrom.* **14**, 1898 (2000).
- [14] B. Anet, M. Lemasle, C. Couriol, T. Lendormi, A. Amrane, P. Le Cloirec, G. Cogny and R. Fillières, *J. Environ. Manage.* **128**, 981 (2013). doi:[10.1016/j.jenvman.2013.06.028](https://doi.org/10.1016/j.jenvman.2013.06.028).
- [15] C. Domeno, A. Rodríguez-Lafuente, J.M. Martos, R. Bilbao and C. Nerín, *Environ. Sci. Technol.* **44**, 2585 (2010). doi:[10.1021/es902735g](https://doi.org/10.1021/es902735g).
- [16] J.R. Kastner and K.C. Das, *J. Air Waste Manag. Assoc.* **52**, 459 (2002). doi:[10.1080/10473289.2002.10470800](https://doi.org/10.1080/10473289.2002.10470800).
- [17] D. Smith and P. Spanel, *Mass Spectrom. Rev.* **24**, 661 (2005). doi:[10.1002/mas.20033](https://doi.org/10.1002/mas.20033).
- [18] G.J. Francis, D.B. Milligan and M.J. McEwan, *Anal. Chem.* **81**, 8892 (2009). doi:[10.1021/ac901486c](https://doi.org/10.1021/ac901486c).
- [19] D. Materić, D. Bruhn, C. Turner, G. Morgan, N. Mason and V. Gauci, *Appl. Plant Sci.* **3**, 1500044 (2015). doi:[10.3732/apps.1500044](https://doi.org/10.3732/apps.1500044).
- [20] C. Guimbaud, V. Catoire, A. Bergeat, E. Michel, N. Schoon, C. Amelynck, D. Labonnette and G. Poulet, *Int. J. Mass Spectrom.* **263**, 276 (2007). doi:[10.1016/j.ijms.2007.03.006](https://doi.org/10.1016/j.ijms.2007.03.006).
- [21] P. Spanel and D. Smith, *Am. Soc. Mass Spectrom.* **12**, 863 (2001).
- [22] D.K. Bohme, G.I. Mackay and S.D. Tanner, *J. Am. Chem. Soc.* **101**, 3724 (1979). doi:[10.1021/ja00508a003.ke](https://doi.org/10.1021/ja00508a003.ke).
- [23] D.B. Milligan, G.J. Francis, B.J. Prince and M.J. McEwan, *Anal. Chem.* **79**, 2537 (2007). doi:[10.1021/ac0622678](https://doi.org/10.1021/ac0622678).
- [24] B.M. Ross, *BMC Res. Notes.* **1** (41), 1 (2008). doi:[10.1186/1756-0500-1-41](https://doi.org/10.1186/1756-0500-1-41).
- [25] P. Spanel and D. Smith, *Med. Biol. Eng. Comput.* **34**, 409 (1996). doi:[10.1007/BF02523843](https://doi.org/10.1007/BF02523843).