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Atmospheric Measurement Techniques Discussions

Interactive comment on "An automated gas chromatography time-of-flight mass spectrometry instrument for the quantitative analysis of halocarbons in air" *by* F. Obersteiner et al.

Anonymous Referee #1

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In this manuscript a specific time-of-flight (TOF) mass spectrometer (MS) (Tofwerk, EI-003) is coupled to a air preconcentration unit with a gas chromatograph separation. This setup is employed for measurements of halocarbons in air. While some GC-TOF-MS studies have previously been conducted, this work describes a TOF-MS model that so far has been rarely used in this application.

This manuscript is timely and describes a promising combination of instrument parts. I find it suitable for amt and recommend publication. However there are several improvements that are required before publication. These are detailed below.

1) Some real air applications and comparisons are missing: An analytical description and performance analysis is the backbone of such an analysis but a real proof by comparison to outputs of other instruments or to real air ambient samples is missing. 2) Even though the experimental work appears sound, many descriptions are confusing and unclear and require a more careful wording and completion with currently lacking information. The description of the nonlinearity is not convincing and needs significant improvement.

Details.

Abstract l. 12, and other places: âĂŽmass trace'. This appears to be a newly-invented expression, which cannot be found in the relevant literature. What is a mass trace? Suggest to replace by an expression that is more common and understandable to the community.

p. 9461, l. 22: The "EI" should be defined when first time appearing, which I believe is same page, l. 20.

p. 9461, l. 21: I suggest to harmonize the spelling TOF MS vs TOFMS. Most of the text uses the latter.

p. 9462, l. 11, âĂŽ... our other GC-MS systems.' References?

p. 9462, l. 26: is the name possibly wrong, shouldn't there be a 'perhydro', so, 'perfluoroperhydrophenanthrene'? and small 'p'.

p. 9462, l. 21, âĂŽ ... ionizer pressure ..'. This is slang, it is not the pressure of the ionizer, suggest to change to something like âĂŽionizer gas pressure', or âĂŽpressure in the ionizer', or similar. Same for âĂŽflight chamber pressure' one the following line.

p. 9462, l. 23. Elaborate more on the quadrupole high-pass filter, can it be adjusted on short time scales (during a single chromatographic run), can it be set to additionally exclued high masses?

p. 9464, l. 1. The description of linearity does not make much sense (...'linear relation of the substance signal in sample vs calibration gas...'). What they author may want to describe is the linearity between injected amounts (mol, gram) and the corresponding signal. Suggest to rephrase accordingly. The sentence starting l. 4 seems unnecessary (except the link to 3.4), it is also confusing, because it somewhat implies that there are techniques of calibrations and comparisons of air samples, for which nonlinearity is not an issue — I don't know of any.

p. 9464, l. 15ff. A simple fact is described rather confusingly due to the notation used. I understand that some of the notation is taken from the literature, but:

m_ac is usually used as the accurate (=measured) mass, indeed a unfortunate definition, and not the accuracy of that! This is fundamentally different. It is the first line (l. 15) of that paragraph that is very confusing and seems unnecessary. I recommend to refraim from the expressions on line15 like âĂŽmass measurement accuracy', and âĂŽaccuracy of a measured ...'. Instead say that the mass accuracy is defined as the relative difference between the measured mass (confusingly referred to as accurate mass, m_ac) and the exact (= calculated m_x) mass, and often expressed in ppm (10-6), then list the formula. Why not stick to text book definitions and explanations. It appears that a simple fact is described confusingly. Or why not use m_meas and m_calc (vs m_ac) to distinguish between a measured and a calculated/theoretical mass?

Additionally some of the literature seems to be also defining the difference between m_ac and m_x the opposite way so that there remains the question of putting the absolute value symbols (|m_ac – m_x |) into the formula, although this is a minor issue.

p. 9464, l. 21: The expression FWHM appears to derive from the literature but I wonder how adequate that had been described and how useful it is here: Why âĂŽfull', what is a âĂŽfull width'? Also, âĂŽhalf maximum'? maximum of what, perhaps the âĂŽheight

signal'? If so, then say so. Otherwise the user is left at interpreting (could also be half area maximum). I am more used to âĂŽwidth at half height' to describe what the authors want to express.

p. 9465, l. 17 and l. 20. Are these arithmetic means based on 'absolute' values of Emac? Figure 2 caption suggest so. If so, this must be said here as it is an absolutely crucial word in this context. The calculations of the mean mass accuracy in 3.1.1 (paragraph 1). yield a miss-leading result and I question their mentioning. What is the usefulness of the arithmetic mean in this context? Leaving it out would also avoid the immediate question that arises as to why the mean target mass mass accuracy is twice that of the calibrant gases. The mass accuracies of individual masses as such are much more important quantities, incl. e.g the ranges they spread. This is nicely described in the second paragraph. However the discussion on the wave-like dependancy on the mass axis (Fig. 2) is missing, a feature that points to some kind of inappropriate fitting routine, e.g. a linear fitting of a non-linear relationship of some sort.

p. 9465, l. 26 âĂŽsystematic and reproducible' distribution. Does this mean that there is a post-correction to the mass errors after the incorporation of all tuning? Otherwise, rather than âĂŽsystematic and reproducible', wouldn't one want to achieve some fitting that yields a âĂŽrandom' distribution of the Emac along the mass axis?

p. 9466, l. 9: please elaborate a little more on the hypothesis of a temperature dependency. Is the instrument not sufficiently thermally insulated? Would this be a problem for field applications? Over what time frame were the 100 ppm observed, from one run to the next (minutes?). How was the experiment designed that lead to the conclusion that there is a strong temperature dependency? Or was this seen already with small temperature fluctuations due to the laboratory air temperature fluctuations? And how was this problem fixed — after all the authors describe that it is a stable system.

p. 9466, para 3.1.2. Suggest to revise this section for improved understanding. Are

'mass resolving power' and 'resolution' used for the same thing? The expression 'the increase' (p. 9467, l. 1) seems unnecessary, even wrong. When using words like 'increase' (dito) or 'relatively' (same line) it must become instantly clear what these words compare to. l. 3, why would the arrival time distribution change?

p. 9466, l. 6 ff. What is the significance of this finding? l. 14: Wasn't this already said earlier?

p. 9470, l. 11: The simultaneous mentioning of 'not linear' and 'has an optimum' is very confusing, suggest to somehow seperate. The 'not linear' is an observed hard fact, but the 'optimum' seems more like a subjectiv choice to be taken, but the way it is used here, it can be mistaken for a 'curve optimum'.

p. 9470, l. 5 ff. This is very confusing when carefully read. Is this comparison of 69 and 68.9947 done with differen mass resolution? Is the 69 measured on an integer basis (maybe that is meant by 'nominal'?). If so, say so, perhaps rather use the expression 'integer', otherwise it can be mistaken by 69.000, in which case this entire paragraph does not seem to make sense. Also, when integer-only masses are measured, what is the mass resolving power (1?), what is used as delta m (0.5, 1?). There are several places in the manuscript and tables and figures, where 'nominal' masses are discussed, and where the discussion is confusing due to the lack of mentioning these details.

p. 9470, l. 22: Conversion to pg/L seems not very useful, after all, 'L' is not a conservative property. Remove sentence ('With the ...'). A more useful quantity would be 'mol'.

p. 9472, p. 3.3: Consider to shorten the introduction to this topic. Is 'precision' and 'reproducibility' used for the same thing? If not clearly define what you mean. For example, l. 9 'reproducibility of precisions' is confusing. Consider only discussing precisions and leaving out (or naming it differently) the discussion on how precisions change over time.

p. 9472, l 26: consider removing the explanation why there is a blank in methyl iodide.

p. 9474 l. 12 'Measurement accuracy...' here is an example of how confusing the descriptions are using the word 'accuracy' with completely different meanings in the same sentence. Also, it appears that this is a rementioning of what was said in the parapgraph above. Why not proceed directly with the discussion of methyl chloroform (not Methylchloroform).

p. 9474, l. 19, 'This ...'. consider removing from here.

p. 9474, l. 26, 'For simplificaton...'. this is confusing, why are integer values used and not those accurate masses, which are ultimately used for measurements with this instrument.

p. 9475, l. 1. Why are precisions poorer in routine ambient air measurement series (compared to repeated standard measurements only)? Is the time spacing the same, i.e. when calculating precisions based on stds only, is it taken into account that the std spacing is narrower. If the precisions are poorer wouldn't this point to memory effects in the system. Why would water play a role, I was under the impression that this was removed from the sample leaving a residual water mole fraction that is similar in air and std samples. (Actually, is it described somewhere if the standards used are 'moist' fillings into cannisters, or dry?). On l. 11, 'moist samples', similar question, I thought the samples were dried.

Section 3.4 Nonlinearity General discussions of nonlinearity and motivations (currently several paragraphs long) should be shortened to a few sentences (remove most of 9475 l. 15 to 9476 l. 17). p. 9475, l. 16: why are the masses of the compounds used. What is more relevant, masses or moles? Consider using ppt and in parenthesis the number of moles.

p. 9476, l. 15, 'For analysis...'. Is this with reference to the experiment following, or a general comment. Also, here 'nominal' masses are discussed, in the experiment, +-0.3

Th are used, is this the same?

p. 9476, l. 20, ‘different volumes of preconcentrated air’ is wrong, once preconcentrated, the volumes are rather similar. Also, it is not apriori clearly said that the variable volume samples are from the same high pressure flask as the standards. Please clarify. l. 21: ‘Variation volumes’ (‘variable volumes’). Why are 0.3 and 0.7 L missing? Was the sequence of chosen volumes random, or was the experiment conducted with monotonically increasing (or decreasing the volume).

p. 9476, l. 28: ‘bracketing’ calibration. If calibration run and standard were alternated, mention this somewhere in the experimental description.

p. 9477, l. 4: The motivation for forming three clases is only motivated by the results found later in the text and leaves the reader in the unknown for a long time, as to why this separation is done.

p. 9477, l. 8 ff: same comments about units as earlier.

p. 9477, l. 25 Observations and explanations on nonlinearities are not convincing to me. Provide more evidence for the observed feature. Name other compounds from the class of high-concentration substances, is e.g. CH3Cl showing the same feature? When looking at figs. 9, it becomes clear that a large nonlinearity is observed at the lower part of the volume range, starting at already 0.1 L with no indication of a decrease of the nonlinearity effect in the range 0.5 L to 0.1 L. There is no indication that below that, the system is linear. I therefore question the explanation and classification into three classes of ppt ranges. Given that CFC-12 is nonlinear at low volumes and noting that 1/5 (i.e. 0.1L/0.5L) of a 500 ppt CFC-12 peak corresponds already to 100 ppt, so the second class of compounds (e.g. CFC-113, CCl4) should show large nonlinearities as well. Please provide graphical evidence of compounds of the middle class. Also, consider merging fig 9 and 11, and most importantly, explain in figure caption, what the differences are (different mass interval). Are there also nonlinearity experiments based on constant volume – variable mole fractions – sampling? What do they show?

p. 9478, l. 2 ff. There is one single sentence on the explanation of the cause of this nonlinearity. Provide more supporting evidence for this hypothesis.

p. 9478, l. 6, ‘the artificial ...’. Report first on the finding of the shoulder before discussing it in more detail. This is the first time the reader hears about the shoulder. Since no evidence is provided that such shoulders exist for other compounds, how do the authors know that this isn’t an interference by another compound with slightly different mass (like the example of CH3CCl3)? Were the nonlinearities conducted with CFC-12 in synthetic air?

p. 9478, l. 25: I find the understating of the observed phenomena by the given explanations rather disturbing.

p. 9479, l. 23. Rather confusing. The accuracy is in most cases not mandatory for high precisions, one can measure very precisely with poor accuracy particularly for halocarbons, where the largest uncertainties derive from the primary reference material.

There is a lot of jargon used in this paper. Some examples given below. This manuscript could benefit from editing by a native English language scientist. p. 9469, l. 29: ‘around 3’. Replace by ‘approximately’, or by an adequat symbol. p. 9470, l. 25: ‘The benefit from going from ...’ p. 9471, l. 12: ‘lie further off ...’, ‘hard to say’ p. 9475, l. 21: ‘from ... upwards ..’ p. 9476, l. 10: ‘when thinking about ...’ p. 9477, l. 19: ‘lay around’. p. 9478, l. 27: ‘a long way to go’.

Chemical compound names are not capitalized in English. Also several are spell in multiple words. Please check entire document. Examples: Figure 8 caption: change Methylchloroform to methyl chloroform (same on p. 9474, l. 10); p. 9471, l. 9: Change âĂŽDichloromethane‘ to âĂŽdichloromethane‘; p. 9462, l. 26 âĂŽPerfluorophenanthrene‘.

Reference list: Needs cleaning up. Muehle with umlaut, chemical formula with number subscriptet. Title of publications with small beginning letters.

Table 1 caption: Maybe re-iterate here that ‘accurate’ means ‘theoretical/calculated’ as the word ‘accurate’ when removed from the admittingly unfortunate definition of ‘accurate’ mass results in confusion. Mention the approximate mole fraction without all the circumstantial explanations and focus on what the results in the table show.

Table 5 caption: It is crucial to mention here what is meant by ‘nominal’ (integer?) and what resolution is used for this integer, and the resolution used in the ‘accurate’ case.

Table 6: Based on which mass resolution? The expression ‘single’ is very confusing. Consider leaving it out. Drift in calibration. State more clearly, over which time these percentage values are calculated. ‘... relative drift in calibration ....’ State more clearly, what kind of drift is discussed,’drift in mass, retention times, ...?’. Same for line 6, ‘Drift in peak area, or mass?” If the drift in the last colum is the decline in peak area for calibration gas, which is alternatingly measured to the air samples, than this is a rather large drift compared to quadrupole-MS, and should be discussed in the text.

Figure 1: Suggest to remove

Figure 2 caption: Possibly, the +-3.47 ppm should be +-0.347 ppm?

Figure 4 Explain what tR is or spell out in the x-axis label.

Figure 7 caption: replace ‘dot’ by ‘diamond’. Maybe add one sentence explaining what conclusion can be drawn from this figure.

Figure 8: What are the exact masses of the co-eluting peak, can you make a suggestion for a compound?

Figure 9 and 11 captions: the most important information is missing (the use of different mass ranges). Consider changing ‘.... relative responses’ to ‘.. volume-corrected relative responses.’

Figure 10, caption: ‘intensity’ in plural.

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