Atmos. Meas. Tech. Discuss., 4, C328–C332, 2011
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Atmospheric
Measurement
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Discussions

Interactive comment on "A field-deployable, chemical ionization time-of-flight mass spectrometer: application to the measurement of gas-phase organic and inorganic acids" *by* T. H. Bertram et al.

Anonymous Referee #1

Received and published: 14 April 2011

This paper describes a new field-deployable time-of-flight (TOF) mass spectrometer, and in particular, focuses on instrumental details pertinent to TOF techniques. As such it could be a useful addition to the literature. However, the title promises much more than the paper actually delivers, to the point of being inappropriate and unacceptable. The paper also has a number of other serious shortcomings and omissions, as detailed below, and will need significant modification before it is acceptable for publication.

General Comments

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When we think of the term ‘measurement’ we think of a systematic demonstration of: 1) sensitivity to an analyte, 2) the ability to calibrate the instrument for the analyte and obtain a reproducible result (hopefully linear but not necessarily), 3) the ability to measure the system background or ‘zero’, and 4) an understanding of the behavior of the analyte on inlet surfaces and perhaps other interference issues. This paper does not manage to do this, even for formic acid. It does demonstrate that formic acid can be detected sensitively and rapidly, and Veres et al. 2008, have covered some of the other issues, so perhaps we can give them formic acid. Not one other organic acid was even identified in the mass spectra. Also, the authors have apparently not seen Roberts et al., 2010 (in this journal) who describe using this acetate ion chemistry for the inorganic acids, HCl, HNCO, HONO and HNO3. Showing a mass spectrum with the proper anion does not mean this system can make a measurement. Any 210Po source/CIMS instrument, configured to measure negative ions, has plenty of Cl-, NO2-, a lot of NO3-, and a number of organic anions in the background of the system. That doesn’t mean it can measure the corresponding acid in the atmosphere.

The way the mass spectra were displayed seems intended to NOT show us what this system can really do. Why not plot the data from 0 to 1000cts (or appropriate number) on a linear scale and the rest of the data on a log scale? This is standard practice for these systems, when one wishes to show the details of signals at low counts. Also, this system has the potential for mass resolution that could be truly revolutionary, but the authors don’t even put tick marks on the mass scale of one figure, and have ticks only every 10 or 20 amu on another, with some ticks on the inside of the panel, obscuring whether or not there is a mass peak there. Suggestion - use a mass scale with ticks at unit amu with the ticks on the outside of the panel.

There are several interesting, important resolution problems that are related to measuring acid anions that this system should be capable of solving, yet none of them are addressed. Let’s start with the 2 ions that are shown in detail, formate and nitrite. Figure 3 shows them at about the same abundance, but more often, especially in the daytime polluted boundary layer, formate is much more abundant than nitrite, to the point that 13C formate (1.1% abundance) will be a significant signal at the nitrite mass (at unit resolution). What a perfect job for a TOF mass spectrometer. Yet the ability of this system to resolve those is not demonstrated. Other examples, just off the top of my head; Mass 85- CF3O- (always there if you use PFA Teflon) and methacrylate, Mass 87- butyrate/pyruvate, Mass 89- lactate/oxalate. I'm sure there are many others.

The data analysis discussion is interesting in that it would be nice to know whether or not all this (supposed) resolving power is available in practical situations, like field measurements. From the discussion of data acquisition and reduction and the fact that the rest of the paper uses unit resolution, the answer appears to be that it is not. In addition, there is only a vague allusion to a mass calibration. Isn't drift of the mass scale one of the central problems limiting the analysis of true high-resolution data? This was not even discussed in this section. These omissions amplify the feeling in the community that this instrument, and the software in particular, is just not ready for extensive ambient measurements in the high-resolution mode.

Acknowledgments – Who supported this work financially? Usually, acknowledgments include a list of funding organizations, strange that this was not done for this paper. Let me be more direct here. It is clear from the list of authors that this work had substantial support from Aerodyne and probably Tofwerk, so in this situation, the companies that make and market the instrument also sponsored the research. There is not necessarily anything wrong with this, but it should be disclosed. Many journals, especially bio-medical journals, have a policy that such arrangements be disclosed, as they represent a potential conflict of interest.

Specific Comments

Title; Unacceptable, how about "A field-deployable, chemical ionization time-of-flight mass spectrometer: application to the detection of formic acid"?

Abstract; All of the specific statements made in the last half of the abstract must be preface by the statement that they apply only to the detection of formic acid.

Pg 1968, Line 2. This sentence makes it sound like H3O+ chemistry can be used with the instrument as it is presented in this paper. My understanding is that the H3O+ ionization scheme, traditional PTR-MS, requires a completely different ion source (cold cathode discharge), and much lower ion flow tube pressures, necessitating the use of a high-field drift tube. It is true that TOF can be used with PTR, indeed there is a commercial instrument available, but the hardware requirements are somewhat different. These aspects must be discussed here is the paper is going to claim this ionization scheme as an option.

Pg 1969, Line 19, I was not familiar with the unit Th, so I looked it up. It should be defined here at first use. Also, my understanding is that, strictly speaking, negative ions should have a negative sign, is that not true?

Pg 1970. In the discussion of the MCP detector, it would be useful to know what the 'dead band' of the detector is. In other words, when a large peak occurs, how long does it take for the detector to recover sensitivity?

Pg 1971. The clustering reaction is nothing new, it has been known for some time that these reactions proceed this way, and in fact cluster decomposition has been used to measure gas-phase acidities by Graul et al., 1990.

Pg. 1971. Collisional dissociation energies scale as E/N (electric field over number density). In fact there is a name for that unit, the Townsend (Td) 1 Td = 10-17 V-cm2. So that is why the authors can state that dissociation probably takes place in the first part of S3. That should be made clear.

Pg. 1975. It would be useful to know how long the signal took to reach a background level when zero air was added. What is the utility in improving formic acid backgrounds when the ambient signal is always well above the background? It seems to me that the uncertainty in the formic acid calibration source is the biggest source of uncertainty

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in this measurement, wouldn't it make more sense to work on that? In addition, the authors will find that backgrounds are crucial factors in the measurement of other acids, such as HONO, if they get around to actually measuring those.

Pg. 1976 Lines19-20. How was the count rate normalized?

Figure 2. This figure is very unclear and must be changed if it is to be acceptable. Does the bottom panel have tick marks? or are those signals? In addition to the above comments about scales, the spectra would be much more clear if the zero counts were offset slightly from the bottom scale.

Figure 3. It looks like from the inset showing formate and nitrite that the peaks have some strange bumps on their leading and trailing edges. What are those? Are they other ions, or is this an aspect of the mass analyzer that was not discussed in the text? This figure appears to not have tick marks at all. The same comments apply to vertical scale and the offset from the bottom scale.

References;

Graul, S.T., M.E. Schnute, and R.R. Squires, Gas-phase acidities of carboxylic acids and alcohols from collision-induced dissociation of dimer cluster ions, Int. J. Mass Spectrom. Ion Proc., 96, 181-198, 1990.

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Interactive comment on Atmos. Meas. Tech. Discuss., 4, 1963, 2011.

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