Miller, Diane M. (CDC/NIOSH/EID)

From: Frank Dean [Frank.Dean@ionscience.com]
Sent: Thursday, December 16, 2010 10:26 AM
To: NIOSH Docket Office (CDC)
Subject: 220 - Components for Evaluation of Direct-Reading Monitors for Gases and Vapors and Addendum
Attachments: NIOSH Components review 101216.pdf

Dear Sir,

I comment upon your draft document reference NIOSH 220, 'Components for Evaluation of Direct-Reading Monitors for Gases and Vapors ' in response to your website inviting public content through December 20th.

Please see my comments attached. Please do not hesitate to contact me if further information or comments would be helpful.

Kind regards

Frank

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Advanced Gas Sensing Technologies

'Components for Evaluation of Direct-Reading Monitors for Gases and Vapors', NIOSH-220.

Review of draft accessed from

http://www.cdc.gov/niosh/docket/review/docket220/pdfs/Components-2010Aug6.pdf

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16 Dec 2010

A note from the reviewer
The focus of this review is on Parts I and II of the above document.

Page viii.
In the title 'Appendix G...' replace 'Programfor' with 'Program for'

Page 1, Column 1.
'The present document, *Components for the Evaluation of Direct-Reading Monitors for Gases and Vapors* (*Components*), further refines the 1995 *Guidelines For Air Sampling And Analytical Method Development And Evaluation* so that it is applicable for evaluating direct-reading monitors for gases and vapors.'

The sentence is confusing in suggesting that new material is refined material. Suggest:

'The present document, *Components for the Evaluation of Direct-Reading Monitors for Gases and Vapors* (*Components*), further refines the 1995 *Guidelines For Air Sampling And Analytical Method Development And Evaluation* and includes an evaluation of direct-reading monitors for gases and vapors.'

Page 3, Column 1.
'log-normal, gamma, etc.': Requires full stop after 'etc.'

Page 6, Column 1.
'**Linearity**
Linearity is the closeness of a monitor's calibration curve to a mathematically defined line.'
'

Suggest '... mathematically defined straight line'

Page 6, Column 1.
'**Response Time**
Response time is the time required for the monitor output to reach a specified value after exposure to a known concentration of test analyte. It is the combination of the lag time (time taken for first detector response to a concentration) and meter response (time to full reading).'
'

This is ambiguous. The time required for full reading in principle may never be quite reached, for example in monitors reliant upon a diffusive process. Moreover the meter response is rarely time limiting.

It would be better, as on page 24 of the *Components* draft, to identify the time taken for a *fraction* of a full scale response, then the more ambiguous time taken for the full scale response is irrelevant, viz,

'**Response Time**
Response time is the time required for the monitor to reach a specified fraction, typically 90 or 99%, of the full scale response. It includes a lag time, the time taken for first detector to first detect a concentration of an analyte.'

Page 8, Column 1.
'Chemicals monitored by conductivity do not need to be in an ionic form in the vapor phase, but may be gases or vapors that form electrolytes by chemical reaction in solution.
'

Should this statement not also embrace other conductivity monitors addressed in following paragraphs:

'... that form electrolytes by chemical reaction in a liquid, or affect the conduting or semiconducting properties of a solid. '

Page 8, Column 1.
'Conductivity measurements are temperature dependent, having a temperature coefficient that can be on the order of 2% per degree Celsius (°C). '

Should read '... of the order'. Temperature sensitivity of these devices varies more than this.

Page 10, after Coulometry section.
Where are Amperometric monitors? Surely this is a very important class of electrochemical monitors which seems to be completely left out of the document.

Page 10, Column 1.
'Pyrolysis produces ions and electrons (e−) that are carried through the plasma to an electrode gap, which decreases the gap resistance and allows current to flow in the external circuit.'

The ions and electrons produced form the plasma, and are carried to electrodes, not to the gap between them.

Suggest: 'Pyrolysis of organics in the gas stream produces a plasma of ions and electrons (e−). Electrodes in the vicinity of the flame collect these, causing a current to flow between electrodes and into an external circuit.
'

Page 10, Column 1-2.
'Reactions in flame ionization... $CH_2 + OH^* \rightarrow CH_2OH^+ + e-$.'

This text does not really emphasize the FID sensing process and the information is possibly not correct. Suggest:

'In the hydrogen flame it is understood that through various reaction pathways a fairly consistent fraction of combustable carbon atoms within the analyte forms cations, probably predominantly as CHO^+'

Page 10, Column 2.
'Flame ionization is a nonspecific detection mechanism ideal for the detection of most organic compounds. The detector does not respond to, or responds very little to, common constituents of air, including water vapor. A potential disadvantage of the flame ionization detector is that electronegative compounds, such as chlorine and sulfur (in the vapor phase), will depress the response, resulting in an underestimate of ambient concentrations. '

Chlorine and sulfur are electronegative elements present in certain volatile compounds. Suggest,

'Flame ionization is a nonspecific detection mechanism ideal for the detection of most organic compounds, including, notably, methane. To some extent it provides a measure of organic carbon content in air, although the presence of electronegative atoms such as chlorine and sulfur in organic volatiles decreases the response of the carbon atom to which it is bonded. [*]. The detector does not respond to, or responds very little to, common constituents of air, including water vapor'

[* see for example, for an excellent review, T.Holm, 'Mechanism of the flame ionization detector II. Isotope effects and heteroatom effects', *Journal of Chromatography A*, **782**(1997), 81-86.]

Page 11, Column 1, **Photoionization**, *first paragraph.*
'...of known constant voltage'

Most photoionization detectors now do not use a constant voltage but rather an RF (radio frequency AC voltage) to illuminate the lamp: delete 'of known constant voltage'. Since the point is for the lamp to be of stable voltage one might replace with 'providing an invariant light source'

Page 11, bottom of Column 1.

$RH + h\nu \rightarrow RH+ + e-$,

where RH is the molecule to be ionized, *hv* is a photon having energy greater than the ionization potential of RH, and RH+ is the ionized molecule.

This is possibly misleading. 'RX' is usually used by chemists to denote a hydrocarbon radical R attached to some group X. So RH denotes a saturated hydrocarbon. The photoionization of RH will proceed mainly as shown for a hydrocarbon, although other charged and neutral fragments may often be produced. Suggest

$XY + h\nu \rightarrow X^+ + Y^-$,

where XY, typically an organic volatile, is the molecule to be ionized, *hv* is a photon having energy greater than the ionization potential of XY, and X^+ and Y^- are ionized fragments, and Y^- is frequently an electron'

Page 11, bottom of Column 1.
'Photoionization detection is a nondestructive technique that can be selective by using appropriate UV lamps of varying energies.'

PID is usually used in an environment in which PID provides sufficient selectivity for one target analyte from many thousands of prospectively sensed compounds. The use of the higher 11.7 eV lamp to access a response from certain compounds not detected by the 10.6 eV lamp is informed by the facts that 11.7 eV lamps are more expensive, less robust and is less selective. Although in principle two lamps might be used to confer selectivity in practice this is not widely offered or employed. So this statement might be deleted, or at least rephrased and placed in a paragraph as suggested below.

Page 11, bottom of Column 1.
'Lamp energies are typically on the order of 10 electronvolt (eV) to 11 eV, but others are available.'

'Lamps providing photons of energy up to 10 electron volts (eV), 10.6 eV (krypton') and 11.7 eV ('argon') are typically offered.'

is more concise perhaps.

Page 11, Column 2.
'PIDs are useful for detection of some permanent gases, such as methane and ethane, but most light permanent gases (hydrogen, helium, nitrogen) have ionization energies higher than 10.6 eV and do not give a response. It is necessary to consider if water will interfere. Monitors incorporating PIDs have traditionally been used as area or survey monitors, but personal PID monitors are now commercially available. While primarily used for the detection of organic compounds, the PID has some utility for inorganic compounds, such as nitric and sulfuric acids, hydrogen sulfide, arsine, and phosphine.'

Contains several errors of fact. Suggest:

'PIDs are useful for detection of most volatile organic compounds containing more than two carbon atoms. The higher the photon energy provided by the UV light source, the more gases are detected. Thus PID containing a 11.7 eV (argon) lamp will detect formaldehyde and many halogenated compounds, not detected by the 10.6 eV (krypton) lamp. While primarily used for the detection of organic compounds, the PID has some utility for inorganic compounds, such as hydrogen sulfide, ammonia and arsine. Permanent constituents of clean air, and methane and ethane are not detected. It is necessary to consider if water will interfere. Monitors incorporating PIDs have traditionally been used as area or survey monitors, but personal PID monitors are now commercially available.

Page 11, column 2
'Under optimum conditions, a PID can detect 5 picogram (pg) of benzene and has a linear dynamic range on the order of 10^7.'

Certainly needs updating. Suggest:

'In the past few years PID has developed significantly. Sensitivity to 1 ng/m3 benzene is now very achievable, engaging cell designs which are resistant to contamination effects [Ion Science 2004*]'

*US Patent 7046012.

Page 11, Column 2 to top Page 12 Column 1.
'The argon ionization detector... linear dynamic range of the argon ionization detector is on the order of 10^3.'

This type of detector is rarely encountered in Health and Safety applications, not least because of the need for a radioactive source. Is it really worth this amount of column? There is much more – and more up to date information - that could be provided on other technologies.

Page 12, Electron Capture.
Electron capture does not necessarily incorporate a radioactive source. An alternative technique engages controlled corona discharge to obtain electrons. With appropriate sample gas conditioning and electrical circuitry, it is possible to obtain sensitive and reliable detection of for example, SF6 by this method.

Page 31 table 1 heading.
'Criteria' should be singular: 'Criterion' (or change other headings to plural: 'Parameters Experiments').