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1st Questionnaire Exemption Request No. 2014 – 1 Response

Exemption for "Cadmium Anodes in Hersch cells for high-sensitivity oxygen sensors"

Abbreviations and Definitions

Cd	Cadmium
NIST	National Institute of Standards and Technology
ASTM	American Society for Testing and Materials

Introduction

Thank you for your questions. Below the questions have been answered as best they could be based on the interpretation of the questions provided. Confidential items are designated by red text.

Question and Responses

Q1: In the application for exemption, a number of examples of industries where Hersch cells are used are specified. Please confirm if these sensors are used for other than industrial monitoring and control purposes?

A1: The instruments containing the Hersch cell are analytical equipment which measure oxygen. There is no other use known for the Hersch cell outside of analytical equipment.

Q2: In the application you mention that "Competing technologies (exempt lead in particular) require calibration at the testing range of interest, for which there are no standards below 10 ppm." Is this to say that calibration of alternatives is not possible at the relevant testing ranges? Please clarify this statement.

A2: The short answer is yes; there is no NIST traceable gas or method to calibrate below 10ppm. A much more detailed answer for this question is located in the appendix of this document. It was drafted by Dan Mayer who is the CTO of MOCON.

Q3: In your application, you clarify that the Cd sensors cannot be replaced in areas where a high level of sensitivity is required of oxygen detection and where stability of the cell is required in terms of the period of reliable performance through which calibration is not required.

a. Please specify if additional parameters are relevant to clarify areas of use where the Cd based sensors are indispensable, including service life of the anode/sensor.

b. Please provide quantitative data to allow understanding the range of implementation in which the use of the Hersch cell is indispensable as well as comparative data for other oxygen sensors, to clarify how the use of the Cd based Hersch cells can be limited to areas where other alternatives cannot be used. If relevant, refer also to how often calibration is required in each technology.

c. In this regard, if other RoHS restricted substances are used in alternatives, please specify the ratio of substance used per device in comparison with the parallel use of Cd in the Hersch cell sensors.

A3-a: We interpret this question to mean the following: the question is asking for additional factors for why the Cd based sensors are essential (factors in addition to high level of sensitivity of oxygen detection and stability of cell / reliable performance through which calibration is not required).

The operation of the Hersch cell has many unique properties which separate it from all other sensors. It does not require reference gases because it is absolute (as described in the appendix document drafted by MOCON's CTO). The Hersch cell is also making a direct measurement of all the Oxygen. The Hersch cell is also designed in such a way that it doesn't need to be recharged over the life of the sensor. The details of this achievement are covered under Patent Number: 5,053,116.

A3-b: Fig. 1 located in the appendix best illustrates the difficulties of measuring with other sensor technologies. All other sensor technologies require that a membrane be present to keep the electrolyte from leaving the sensor. When the membrane is present the sensors no longer directly measure all of the oxygen. This requires that the sensor be calibrated.

To accurately calibrate the sensors a NIST traceable gas must be used. As of October 8, 2014 the lowest NIST Standard Reference Material which is available for purchase from NIST is 2 Mole % (20,000ppm). There are a few gas manufacturers who can make a lower value but it must go through NIST's NIST Traceable Reference Material (NTRM). The manufacturer must make at least ten tanks which follow a NIST Traceable process. The data is sent to NIST and verified. The lowest NIST has seen done with this process is 10,000ppm +/- 1% relative with the most common level made being 210,000ppm. There are some manufacturers who claim they can make a NIST traceable gas down to 10ppm but when MOCON contacted NIST they stated they have never seen a gas that low. Therefore these claims of 10ppm are suspect. Even if it was possible to dilute the 10,000ppm gas below this concentration the +/-1% relative uncertainty would be multiplied down to the level of measurement.

Fig. 1 shows the impossibility of calibrating at a level which is 100,000,000 times lower than the best calibration gas available. The chart shows that if the instrument was calibrated at 10,000ppm the +/- 1% error in the stated value would be multiplied over almost 8 magnitudes. Therefore any technology that would rely on a calibration at that level to measure almost 8 magnitudes away would be so inaccurate the measurement would be invalid.

The chart shows the progress MOCON has made with the Hersch cell since the original invention in 1961. In 1978 The Hersch cell had a sensitivity of 0.1 $cc/m^2 \cdot day$ (34.7ppb). Over the next 53 years improvements were made to achieve much lower levels of sensitivity. Currently the sensor has enough sensitivity to see 0.001 $cc/m^2 \cdot day$ (0.347ppb). Even at this level we have customers who would like to see even lower. The OLED and Solar panel industries would like to measure ten times lower than that at 0.0001 $cc/m^2 \cdot day$ (0.0347ppb). To get to this point it will take at least another three years of research and development.

There are other technologies which have been researched but they too have their own limitations. In fact MOCON uses several of these other technologies in other less sensitive instruments. They include Pb, ZrO_2 and Optical Fluorescence. These technologies all measure oxygen as low as single ppm levels and all require frequent calibration with certified gases.

Other technologies have been researched but have been met with their own limitations. These include Tunable Laser Diodes, Pb, ZrO_2, other electrochemical sensors and Optical Fluorescence. They all have to be calibrated because there is no direct measurement of oxygen taking place.

A3-c: It should be emphasized that **if** other RoHS restricted substances were used the most likely candidate would have a ratio nearly 1:1 to the current Cd use. This is because the path length needed to achieve 100% reduction would still need to be maintained. Dan Mayer's comments in the appendix detail this too.

Q4: You mention that MOCON Inc. are currently the only supplier of the technology for which the exemption is requested. Please confirm if this statement is made in relation to the global market or to the European market. If relevant, please provide a list of other manufacturers of this technology on the global market.

A4: To the best of our knowledge MOCON is currently the only supplier of Cd based Hersch cell Sensors for the global market.

Q5: The application contains some information for various alternatives, aimed at showing that substitution with such alternatives is not practical. It is furthermore stated that it cannot be confidently stated that an alternative exists. Please clarify if research is being undertaken to find substitutes for replacing Cd in this application (other compounds) or to develop technologies that would eliminate the need to use Cd. In this regard, please detail what stages such research requires to clarify how much time would be needed once an alternative candidate was found. In this regard, please also refer to research efforts targeted at reducing the amount of Cd needed per anode/plaque.

Q6: The information provided for alternatives is mainly based on the ERA report from 2006[2] and only refers to substance alternatives. Please also detail if other technologies can be used that would eliminate the need for using the anode, thus eliminating the need for Cd.

A5&6: It is believed questions 5 and 6 are best answered together because they tie so closely to each other. MOCON is continually searching for other methods to improve our sensors. This was addressed at the end of Dan Mayer's section named "Changing anode Material Problem". It details how MOCON has researched several different anodes. None of which have had any success when compared to the performance of the Cd based sensor.

Most of the other sensors require a barrier membrane to maintain the electrolyte. To get the sensor to last the electrolyte needed to be protected with a membrane. As soon as the membrane is introduced the sensor needs to be calibrated. The membrane also brings up the direct measurement vs indirect measurement. Fig. 2 in the appendix demonstrates the difference between the two different designs. With a membrane the sensor is no longer reducing all oxygen molecules at the anode because a majority of the oxygen molecules pass over the membrane.