JBCE answer to Questionnaire 2 (Clarification)

Exemption 1a of RoHS Annex IV

30th July, 2021

As an applicant, JBCE would like to answer the questions dated on 22nd July.

Please kindly find our answers in the attached.

If you have any further questions, please do not hesitate to contact to us.

We are looking forward to continued contribution during the consultation phase of evaluation.

Yours sincerely,

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ABOUT JBCE

Founded in 1999, the Japan Business Council in Europe (JBCE) is a leading European organization representing the interests of about 90 multinational companies of Japanese parentage active in Europe. Our members operate across a wide range of sectors, including information and communication technology, electronics, chemicals, automotive, machinery, wholesale trade, precision instruments, pharmaceutical, textiles and glass products.

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Questionnaire 2 (Clarification) Exemption 1a of RoHS Annex IV

Wording of the Requested Exemption:

Lead in the stem glass of pH glass electrodes and ion selective electrodes equipped with a pH glass electrode with complex shape as following.

1. Micro Type pH Glass Electrode

Composite electrode that has a spherical or tube-shaped pH responsive glass membrane with a diameter of 4.0 mm or less and a reference electrode with a liquid junction at a position vertically within 6.5 mm from the tip.

2. Flat Type pH Glass Electrode

pH glass electrode with a flat pH response membrane at the tip of a glass tube with a diameter of 6.0 mm or more.

3. Needle Type pH Glass Electrode

Composite electrode that has a conical pH response membrane with a tip angle of 40 ° or less and with a diameter of 10 mm or more.

Requested validity period: *7 years*

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1. Acronyms and Definitions

ISFET	Ion Sensitive Field Effect Transistor
Pb	lead

2. Background

Bio Innovation Service, UNITAR and Fraunhofer IZM have been appointed[1] by the European Commission through for the evaluation of applications for the review of requests for new exemptions and the renewal of exemptions currently listed in Annexes III and IV of the RoHS Directive 2011/65/EU.

[1] It is implemented through the specific contract 070201/2020/832829/ENV.B.3 under the Framework contract ENV.B.3/FRA/2019/0017

You submitted information to substantiate your request for the renewal of the above-mentioned exemption. This information was reviewed and as a result, we ask you to kindly answer the below questions for further clarification of your request until 28 July 2021 latest.

3. Questions

1. You stated that lead is added to the stem glass to alter its characteristics in a way that it can be joined with the pH responsive glass during manufacturing of the complex shaped electrodes you described (micro, flat, needle type).

    a. Are there any substances other than lead that may fulfil the same function in the stem glass? What is the status of research that has been carried out in this respect?

    To the best of our knowledge, there are no examples of research for adding other elements in a stem tube that can achieve the same functionality as lead. The glass of stem tubes used for pH electrodes is commercially available product for a wide range of applications, not dedicated to pH electrode application. The development of stem tubes dedicated to pH electrode is not feasible for a large-scale production because the demand of pH electrode is far smaller than demand for other applications.

    Therefore, a glass responsive membrane that can be adapted to commercially available stem glass is being developed.

    b. One European manufacturer of pH electrodes has stated that they have transitioned from lead glass to barium glass to manufacture electrodes including flat membrane electrodes. Please provide reasoning on why this has not been done in your case, including evidence where available (data, measurements, images, etc.).

    Barium is one of the general additives when making the glass, so we believe the main purpose of adding Barium is not to achieve the same functionality as lead. (Please kindly refer the attached appendix in detail)

    We do not have any information exactly who is the supplier of pH electrode with lead free, but Barium. We are happy to investigate further, if you could give us the information of the manufacturer or product which you refer.

2. You have discussed ISFET electrodes as an alternative technology to glass electrodes. You have stated that one disadvantage of ISFET is that the shape cannot be completely flat. It appears that some suppliers offer pH sensors with ISFET electrode and flat tip, for instance (non-exhaustive examples) Alphaomega[2] or Horiba[3].

    a. Please provide reasoning and evidence to support your statement that ISFET cannot be completely flat, taking into account the examples of products advertised as flat ISFET electrodes.

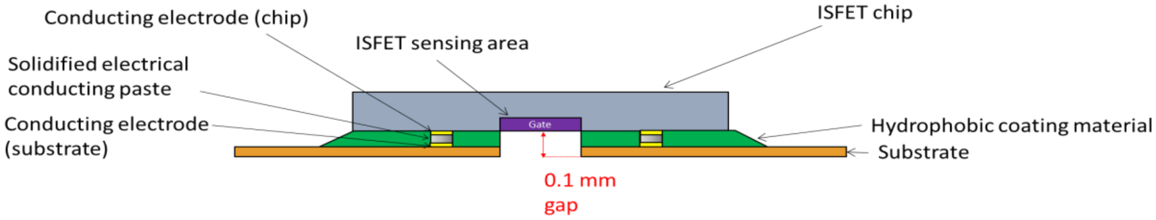
[2] https://www.alphaomega-electronics.com/en/electrodes/4599-0040-10d-laqua-electrode-ph-isfet-ion-sensitive-field-effect-transistor.html

[3] https://www.agriculturesolutions.com/horiba-flat-isfet-ph-electrode-0040-10d

An ISFET chip is fabricated using a conventional MOS(Metal-Oxide-Semiconductor) process. In order to building a field-effect transistor such as an ISFET on the top of the electrode, it is required to locate the sensing area and conducting electrode (the terminal to take out the electrical signal from a field effect transistor) on the same surface.

Sensing area must be in contact with the measured samples (typically water) but, on the other hand, conducting electrodes must be kept strictly isolated from liquids to protect the sensor against malfunctions.

This protection is typically performed by depositing a thin layer of a hydrophobic coating material, as it can be seen on the fig below.



The sensing area of the ISFET chip is consequently around 0.1 mm depth the level of the substrate.

While the gap of 0.1 mm might be considered small compared to previous generation of ISFET products, this cannot prevent the formation of air bubble on the top of the sensing area during measurement. Air bubbles can be ultimately removed by stirring the solution. However, since there are some applications in which it is impracticable to stir during measurement, an ISFET pH electrode is not always an alternative to glass pH responsive electrode due to the 0.1 mm gap existing on the top surface of ISFET pH electrode.

b. In general, can ISFET electrodes be designed to measure the pH of applications that currently need the flat, microelectrode, or needle type glass electrodes for which the exemption continuation is requested? In other words, can pH meter fitted with an ISFET electrode carry out the same measurements as pH meter fitted with flat, microelectrode, or needle type glass electrodes, besides the disadvantages of ISFET you have stated (e.g. narrow measurement range, resin body, etc.)?

It might be technically possible. However, the microelectrode design cannot accommodate the ISFET chip that is bigger than the 3 mm diameter of the pH sensing area. We address that the flat electrode cannot be done perfectly flat using ISFET for reasons explained on the previous point.

3. Concerning another disadvantage of ISFET electrodes, you stated: "*ISFET has a resin body, which can be damaged by organic solvent, chlorine and other chemicals that can permanently damage the ISFET chip*".

   a. Are both the body and the chip susceptible to permanent damage? Through which type of substances, respectively (substance type and examples)?

We would like to share our best knowledge of the permanent damage in relevant to ISFET chip as follows.

1/ ESD

A pH-sensor based on an ISFET chip is very sensitive to electrical static discharges (ESD) such as every Field-Effect transistor-based technology. Unlike most integrated circuits, which are operating in a closed, well-protected, environment, ISFET are often exposed to very high intensity ESD events. For example, very low conductivity waters or hands of someone manipulating the pH sensor can generate ESD events of dozens of kV that may deteriorate permanently an ISFET chip.

Despite ESD-protection integrated in the ISFET pH sensor, some applications are not suitable for ISFET due to the high occurrence of ESD-events.

On the other hands, glass-made pH electrodes are totally insensitive to ESD.

2/ Alkali solutions

The sensing layer of an ISFET is a metal oxide (for example, Al_2O_3 or Ta_2O_5) deposited during the CMOS process. Despite being chemically inert in most aqueous solutions, metal oxide materials will be dissolved in highly concentrated alkali solutions (such as 1M NaOH or KOH), with a etching rate increasing exponentially with the temperature.

3/ Organic solvents

The body of the pH sensor, the substrate of an ISFET chip or the hydrophobic coating used to protect the ISFET connection can be damaged by long exposure in organic solvents.

b. Why are plastics used for the body of ISFET electrodes? Are there other materials in use, or may be used, such as ceramics, glass, or other substances that may be more resistive to substances discussed in your response to question 3.a? If not, could you explain why not?

In the encapsulation process of the ISFET sensor, the ISFET chip and several additional components (such as a glass thermistor or a SMD capacitor) are mounted directly inside the plastic body, which has been designed on purpose to fit each component.

This would be probably extremely difficult to fabricate a ceramic-based body that can accommodate such a complex geometry with the tolerance on size and the reproducibility that can be achieved with the current polymer body.

We also believe that glass might not be suitable because some steps of the encapsulation process require some mechanical constraints on the sensor that can ultimately break a glass material.

c. Some products fitted with an ISFET electrode employ materials such as PEEK (Polyether ether ketone), FFKM (perfluorinated rubber) and ceramics[4]. Do such products also have issues with damage from organic solvents and other substances that you described previously?

We agree that polymer materials you proposed can increase the chemical resistance for the body of the ISFET pH sensor, although some fluorinated materials may not bonded with adhesives.

On the other hand, we believe that changing the material of the sensor body will not be effective to overcome essential issues of the ISFET which are ESD events and low lifetime in strongly alkaline solutions.

In addition, changing the material of the body will not remove the requirement of using a hydrophobic coating material in order to connect the ISFET chip with the substrate. A coating material will not have increased chemical resistance by changing the material body.

ISFET pH sensor made with a PEEK or a FFKM body will certainly share most of limitations in the ISFET technology we stated earlier in this document.

Please note that answers to these questions will be published as part of the evaluation of this request. If your answers contain confidential information, please provide a version that can be made public along with a confidential version, in which proprietary information is clearly marked.

[4] One such example may be: https://www.de.endress.com/en/field-instruments-overview/liquid-analysis-product-overview/pH-digital-sensor-cps47d (last accessed: 8th July 2021)

Appendix: About the effect of adding barium (Ba) to the stem glass material

Alkaline metal elements and alkaline earth metal elements are generally added in a glass material as “modifiers”. Modifiers facilitate the production by improving the workability of the glass but also allow adjusting some glass properties such as the coefficient of thermal expansion or the chemical durability. One of the most commonly added elements to glass is Ba, as a “glass modifier” (Table 1 is taken from the Glass Engineering Handbook).

Table 1: Classification of glass-forming inorganic substances

Glass-network formers	Glass-forming intermediates	Glass modifiers
SiO_2	TiO_2	Li_2O
B_2O_3	TeO_2	Na_2O
P_2O_5	Al_2O_3	K_2O
GeO_2	Bi_2O_3	MgO
BeF_2	V_2O_5	**BaO**
	Sb_2O_3	CaO
	PbO	SrO
	CuO	LiCl
	ZrF_4	NaCl
	AlF_3	BaF_2
	InF_3	LaF_3
	$ZnCl_2$	
	$ZnBr_2$	

Since glass modifiers have weak bonds, metallic cations (such as Ba) can diffuse inside a glass during the high temperature fabrication process but will not contribute in bridging the glass network. On the other hand, “glass forming intermediates” such as lead oxide (PbO) are essentials for the formation process of glass. Lead cations (Pb) act as bridges in the glass network for the diffusion of different kinds of others elements by heat during the formation of the glass. PbO is therefore essential to bond glasses with different thermal characteristic, such as a relatively large variability in thermal expansion coefficient. As we shown in the table above, Ba is classified as a “modifier”, not as a “Glass-forming intermediate”. Ba does not have the same function than Pb in the glass.

We also would like to address that PbO is essential to bond glasses with different thermal characteristic, such as a relatively large variability in thermal expansion coefficient. This is always the case between response glass membrane and the stem glass.

In comparison to other glass-forming intermediates listed in the above table, we summarized the necessary properties and specific negative impact in case of pH electrode application. (Table 2)

Table 2: Comparison of glass-forming intermediates in necessary properties

	pH sensitivity	Alkaline error	Water proof	workability	Other disadvantages
Al_2O_3 Bi_2O_3 Sb_2O_3 AlF_3 InF_3 $ZnCl_2$ $ZnBr_2$	Low sensitivity	Cause of error	No negative impact	No negative impact	N/A
V_2O_5	No negative impact	No negative impact	Less water proof[1]	No negative impact	N/A
CuO	No negative impact	No negative impact	No negative impact	Less workability	N/A
TiO_2 TeO_2 ZrF_4	No negative impact	No negative impact	No negative impact	No negative impact	Cause of less formability
PbO	No negative impact	No negative impact	No negative impact	No negative impact	N/A

[1] Please refer "Effect of Sb2O3 Addition on Water Durability of V2O5-P205 Glass" https://www.jstage.jst.go.jp/article/jcersj1988/100/1161/100_1161_685/_pdf