CoGDEM

The Council of Gas Detection and Environmental Monitoring

www.cogdem.org.uk

Final Response to Consultation for PFAS Fluoropolymers Used in Gas Sensors

Contents

0. General Comments

Proposed Derogations

On 13 January 2023, the competent authorities of five EU/EEA states (“Dossier Submitters”) submitted to the European Chemical Agency (“ECHA”) the PFAS REACH Annex XV Restriction Report (“Proposal”). The Proposal covers all PFAS and their uses, including in all Gas Sensor applications.

Who is CoGDEM?

The Council for Gas Detection and Environmental Monitoring (CoGDEM) was founded in 1974 by the UK's leading gas detection manufacturers as a trade association; CoGDEM’s activities are wholly financed by its members . CoGDEM is the co-ordinating body of the gas detection, gas analysis and environmental monitoring Industries, representing the collective interest to Government, EC Commission, BSI, and other trade and professional bodies.

An original objective was to be represented on BSI committees involved in gas detection and to address issues raised by the Coal, Electricity, Gas (CEG) committee's draft gas detection standard. CoGDEM joined BSI committee GSE/29 (now EXL/31/1) which created BS 6020 for flammable gas detectors.

CoGDEM now sits on the sub-committees that have worked, or continue to work on flammable and toxic gas safety and air quality standards. CoGDEM is represented on CENELEC, ISO and IEC committees , drafting documents used to create EN and global IEC and ISO standards. CoGDEM has good relations with the UK Health & Safety Executive (HSE) and others, and contributes to reducing the number of incidents and improving the standard of available gas detection equipment for both industrial safety and domestic CO alarms in residences.

CoGDEM membership includes more than 50 companies (www.cogdem.org.uk); most of the member companies have global sales networks and many have multinational manufacturing sites.

CoGDEM have engaged the services of Graham Wardman of SSC Consulting Ltd, to make this submission (and the later submission in September) on their behalf.

Objectives of this Report

To present data from the Gas Detection and Environmental Monitoring Industries on the usage of PFAS chemicals and materials within the range of Gas Detectors and Environmental Monitoring equipment sold by Companies within the Trade Industry.

We have used this data from our members to present a derogation listing by PFAS chemical family, for inclusion in the full Socio-Economic review in September.

1. Sectors and (sub-)uses

Gas sensors, gas detectors and domestic CO alarms do not fit neatly into a single sector. The critical PFAS materials are fluoropolymers, specifically expanded PTFE (ePTFE), solid and powder fluoropolymers and fluoroelastomers.

The most relevant sector is *Medical devices* with sub-use *Diagnostic laboratory testing*.

An alternative sector is *Energy sector*, with sub-uses *Proton Exchange Membrane (PEM) fuel cells* and *Electrolysis technologies (not PEM)* being relevant to the internal construction and mechanism for certain types.

Annual usage of fluoropolymers in Europe for gas sensors, gas detectors and domestic CO alarms is <10t/y, which is less than 0.015% of the EU usage of 75,000 t/y of fluoropolymers.

2. Emissions in the end-of-life phase:

Identity of the Substances

The PFAS materials used in the gas sensor/detector industry are exclusively confined to the subset known as fluoropolymers (FP) defined in as '*a carbon-only polymer backbone with F atoms directly attached to it, though some fluoropolymers also have Cl or O directly attached to the backbone*'.[1]

Two recent RMOAs (Risk Management Options Analysis) [2,3] recommend that exemption of FPs from the proposed ECHEM restrictions is warranted due to their low hazard and low risk because '*substances containing only a -CF2- group are not considered to degrade to arrowheads that have given rise to the environmental and/or human health concerns about PFAS'* [2], due to the absence of reactive functional groups. Further, it is strongly argued[4] the lack of sound scientific evidence of '*insignificant environmental and human health impacts*', is entirely in line with the definition for Polymers of Low Concern (PLC) as defined by the Organization for Economic Cooperation and Development (OECD) definition[5].

However even for a PLC compliant substance, emissions harmful to human health and the environment could still arise during manufacture, use and eventual disposal[6]. In the case of FPs, these life cycle emissions exist in a fast-changing landscape as abatement technologies to remove any polymerisation aids based on the non-polymer PFAS of that provoked the regulatory action are developing rapidly, along with greater understanding of incineration conditions for safe disposal[7]. This section addresses these life cycle emissions starting at receipt of supplied FP parts to the factory, covering the following finished articles (depending upon the Manufacturers product offering:

(a) Gas Sensors -gas sensors/factory test appliances

(b) Appliances - devices with embedded gas sensors, namely, domestic CO alarms and industrial gas detectors

Further to this definition, it means that CoGDEM Gas sensor/detector manufacturers fall into three broad categories:

(i) manufacturers of sensors who supply to gas detector/alarm companies

(ii) manufacturers of gas detectors/alarms who manufacture their own gas sensors, and

(iii) manufacturers of gas detectors or CO alarms who purchase gas sensors.

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[1] Buck, R. C et al, *Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment : Terminology, Classification, and Origins. Integr. Environ. Assess. Manage.* 2011, *7* (4), 513–541.

[2] UK HSE, ***https://www.hse.gov.uk/reach/assets/docs/pfas-rmoa.pdf***

[3] Plastics Europe, *Regulatory Management Option Analysis for Fluoropolymers* (2022) ***https://fluoropolymers.plasticseurope.org/index.php/fluoropolymers/irreplaceable-uses-1/reports-policy-documents/rmoa.pdf***

[4] Henry, B. J; Carlin, J. P; Hammerschmidt, J. A; Buck, R. C; Buxton, L W.; Fiedler, H.; Seed, J.; Hernandez, O. A Critical *Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers*. Integr. Environ. Assess. Manage. 2018, 14 (3), 316−334

[5] OECD Task Force on New Chemicals Notification and Assessment. *Data Analysis of the Identification of Correlations between Polymer Characteristics and Potential for Health or Ecotoxicological Concern*; Paris, 2007

[6] Lohmann, R et al; *Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS?,* Environ. Sci. Technol. 2020, 54, 12820−12828

[7] Sales, J.; Hernández, F.; Kapoor, D; van den Noort, M; *Fluoropolymers: The Safe Science That Society Needs-*, International Chemical and Law Review, 2022

The process of making gas sensors is common to all three categories and we treat it as such for the purpose of emissions (Table 1). We consider emissions in three phases of the life cycle:

- **Manufacture** of finished articles
- **Use** in the field.
- **Disposal** at end of life covering landfill, incineration and recycling

Raw Materials

Manufacturing and forming of FP materials are omitted from our analysis because FP manufacturers have made their own submissions to ECHA which, due to proprietary knowledge, they were unable to share with us. Emissions during raw material manufacture are therefore already covered, and should we try to enter values here, we would run the risk of double accounting as well as providing potentially erroneous values.

In the discussion that hereby follows, all quantitative data is based on replies from CoGDEM members to a detailed questionnaire.

Manufacture of Finished Articles

For the gas sensor/detector industry (especially the highly dominant amperometric electrochemical gas sensor sector), PTFE is by far the important FP and is supplied in a variety of forms (Table 1); it has been integral to these gas sensors since their inception in the 1960s[8]. FPs of lesser usage in the sensor construction are PVDF, PFA, FEP, fluoroelastomers (FKM, FFKM, Viton™, Kalrez ™) for seals/gaskets in the gas sampling lines, and perfluoroether polymer-based greases, used as internal sealants in electrochemical gas sensors.

Materials usage (kg)	Gas Sensor specific PFAS					General Purpose Fluoroplastics		
	ePTFE	Dust filters	Solid PTFE	PTFE powder	Fluoro-ether grease	Gas tubing	Machined plus moulded	Fluoro-elastomer gaskets
TOTAL CO Sensors	3443	435	0	41	0	0	0	0
TOTAL Gas Sensors	4995	612	595	473	135	224	73	2300
TOTAL Gas Detectors	0	324	127	0	104	5847	1245	4117
GRAND TOTAL kg	**8438**	**1371**	**722**	**514**	**239**	**6071**	**1318**	**6417**
SUMMARY kg			**10531**	**7903**	**239**			**6417**

Table i Table 1: Annual global usage of FP materials in the Gas Sensor and Gas Detector industry for 2022

Table 2 shows how the different FP material parts are represented in the three product categories of gas sensors, gas detectors and domestic CO alarms. Feedback from members is that the industry uses two main major suppliers for ePTFE and dust filters and one supplier for PTFE powders. This avoids the issue of variability in PFAS impurities; for the same FP part, purity levels will depend on the individual supplier's manufacturing processes[6].

[8] See e.g., *The Mechanism of Operation of the Teflon-Bonded Gas Diffusion Electrode: A Mathematical Model*, J. Giner and C. Hunter, 1969.

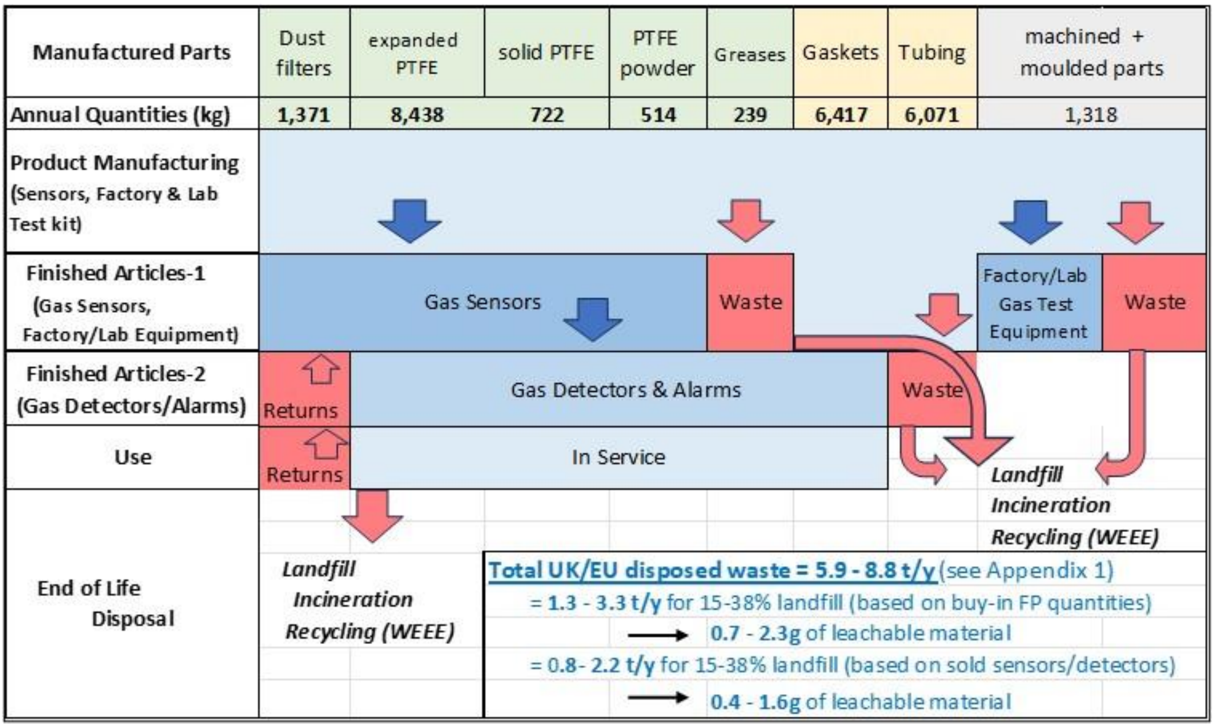

Table ii Materials flow diagram highlighting the different stages in the life of the FP materials. Blue arrow signifies product, Red arrow signifies waste or warranty returns.

The gas sensor/detector manufacturing process operates stringent safety measures to protect workers from the release of the hazardous electrolyte liquids, toxic lead (Pb for oxygen sensors) anodes, and poisonous or explosive gases. Also of particular importance is that materials are carefully selected on the basis of low outgassing (release of volatiles); otherwise, the sensor performance is compromised, e.g. generation of bubbles in the liquid electrolyte of amperometric electrochemical gas sensors. PTFE has a history as a material of choice for NASA due to low outgassing amongst other properties[9].

Manufacture of Gas Sensors (a)

For the gas sensor manufacturing process, the as-received FP parts are either used unchanged from the *as received* state or *processed further.*

Parts are mostly used unchanged, the exceptions being fabrication of the electrodes and a sealing step, both of which involve stamping out membranes from supplied sheets and heating during electrode manufacture. All heating is done under extraction and at temperatures in excess of 150°C but below 327°C, the melting point of PTFE, ensuring the structural form of the parts are retained. Fabrication of the electrodes is a highly specialised operation, critical to the sensor performance. It is usually a 2-step process involving sintering (250-310°C) a mixture of catalyst and PTFE powder, followed by depositing onto an ePTFE membrane. It is the unique characteristics of this optimised 3-component assembly that enables the sensor to function[10]. Release of entrapped monomers or oligomers of $[CF_x]_n$ may occur during sintering and would be removed by the oven extraction system. Sintering is a process used by five of the CoGDEM members, and each will use company confidential

[9] https://standards.nasa.gov/sites/default/files/standards/KSC/C/0/KSC-KTI-5210C.pdf

[10] LIFE SAFETY DISTRIBUTION GmbH; 1ST Public Consultation (22 March – 25 September 2023)
Request for exclusion or derogation of certain fluorinated materials used in gas sensor applications from the PFAS REACH restriction Proposal.
Table of

heating profiles and the process of sintering the electrode and forming the catalyst structure onto the ePFTE as single or combined processes is also company confidential. Setting aside those parts contaminated by contact with the catalyst and the electrolyte, the supplier's Safety Data Sheet is valid during the gas sensor manufacturing process.

The sensor is assembled by stacking the component parts in a specific order in a small cylindrical plastic (non-FP) pot, done automatically or manually with workers using appropriate protective clothing and tweezers for handling the parts. The pot is sealed as a final step with only the dust filter exposed to the external atmosphere, meaning that most of the FP parts are encased. For sensors assigned to detecting flammable or explosive gases, an additional process step embeds the sensing components in a specialist metal housing with flame-retarding properties.

This manufacturing sector operates a just-in-time production model so stock is always kept minimal.

Manufacture of Factory/Laboratory Appliances for Testing Gas Sensors

In the second category of finished articles (a), namely, gas sensors, preformed or machined FPs are used as production tooling to hold arrays of gas sensors during testing. It is general practice to clean machined parts before first use, typically involving degreasing in an ultrasonic bath followed by baking the entire assembly at 110 - 150°C to finish driving off possible contaminants.

We conclude that PFAS emissions of concern do not arise during the sensor or test appliance manufacturing phases.

Product Scrap and Returned Gas Sensors: Sensors that failed or scrapped during manufacture/ test or returned by customers vary in total between CoGDEM members from 0.5% (lowest case) to 6% (highest case). The dominant procedure is not to dissemble the sensors but simply to dispose of them as hazardous waste, due to contamination by the electrolyte (and Pb for galvanic oxygen sensors). Specialist metal refineries (e.g. Johnson Matthey) can recover the metal catalyst and dispose of the (mostly non-PFAS) polymer housing. Disposal as hazardous waste at treatment centres must be in line with guidelines under Article 8 of the WEEE Directive 2012/19/EU[11], which outlines the criteria for specific materials and components. For incineration protocols, all PFAS materials should be incinerated at temperatures in the range 850°C-1100°C[12] with proscribed residence times, causing cleavage of the C-F bond by hydrogen radicals[13,14]. In this way, the PFAS is mineralised to HF and CO_2. Emitted acid gases are scrubbed in stacks (usually using calcium compounds) that are properly designed and maintained.

Manufacture of Gas Detectors and Domestic CO Alarms (b)

These processes are best described as assembly and calibration operations. For gas detectors, the gas sensor is a component that is connected to custom electronics embedded with the company's firmware, and typically includes an LCD/OLED display, audio alarm and if portable, batteries all of

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[11] Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE) Text with EEA relevance

[12] *Lallas, P L. (2001). The Stockholm Convention on Persistent Organic Pollutants American Journal of International Law. 95 (3): 692–708. doi:10.2307/2668517. ISSN 0002-9300. JSTOR 2668517. S2CID 144521094.*

[13] Aleksandrov, K et al; *Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas* Chemosphere 226 (2019) p898-906 DOI: 10.1016/j.chemosphere.2019.03.191

[14] Taylor, P H.et al; *Investigation of waste incineration of fluorotelomer-based polymers as a potential source of PFOA in the environment*, Chemosphere 110 (2014) p17-22 DOI: 10.1016/j.chemosphere.2014.02.037

which are encased in a non-PFAS plastic enclosure. FP tubing and gaskets may form part of the assembly for some gas detectors.

As with (a), we conclude that PFAS emissions of concern do not arise during the gas detector/ CO alarm manufacturing phase.

Product Scrap: For those respondents that replied, the combined manufacturing scrap and warranty returns are typically <1%. As with finished article (a), we assume that PFAS components specific to gas sensors will be incinerated as hazardous waste while tubing and gaskets are treated as non-hazardous waste and disposed as landfill waste.

Use Phase

During use, the sensors are enclosed inside devices, modules, monitors, and other various instruments Wear and tear does not occur within these enclosures. The sensor is designed to operate up to 50-60°C so will not be subjected to temperature extremes over its working lifetime of 2 – 5 years.

We can conclude that FPAS emissions of concern do not arise during the product use phase.

End of Use Phase

UK and EU wide regulations under the WEEE Directive require disposing domestic CO alarms (a consumer product) at local recycling centres. Equally, end-of-use procedures for industrial detectors follow the disposal guidelines under the same WEEE Directive.

Of the three phases covered here, article manufacture, product use and end of life, it is end of life where emissions could occur. There is currently no legal obligation to recycle and so when products enter the waste management stage, they are either incinerated or go into landfill. In Appendix 1, the total FP tonnage going to disposal is calculated to be in the range 5.9 – 8.8 t/y (Appendix 1).

According to Annex XV of the Restriction Report[15], *Plastics Europe* estimates 80% of fluoropolymer waste goes to incineration and only 15% to landfill, while European waste statistics for 2018 suggest landfill waste is as high as 38%.

As mentioned earlier, incineration municipal treatment centres using the correct firing conditions and with appropriate scrubbing can prevent PFAS emissions arising[14]. This of course places the onus on these regulated treatment centres to be rigorous in operating to the required protocol and in maintaining their incinerators.

This leaves landfill as the primary source of waste emissions. Studies on leachable material have focussed on PTFE fine powders with <1 ppm being quoted in the most recent work for a 'wet' state[5]. Fine powders have by definition high surface areas for contact with the surrounding environment whereas most PTFE waste is lower in surface area, e.g. dust filters, ePTFE membranes, solid membranes. Furthermore, fine powder features only in making the sensing electrode and will have undergone coarsening, resulting from the sintering step. They will be delayed in interacting with the environment due to the time taken to degrade the outer plastic pot (polycarbonate or acrylonitrile butadiene styrene (ABS)) – here we are assuming that under WEEE, the gas sensors will be removed from the detectors/alarms for separate disposal. t is worth noting that the PTFE powders are present in only 3 of the 5 sensor product categories (Table 3, Appendix 1), giving a weighted average of 17.7% when volume of UK/EU sales for each sensor type is taken into account. So, the available information

[15]. ECHA (2019b): Annex XV Restriction Report. Proposal for a Restriction: *ANNEX XV RESTRICTION REPORT – Per- and polyfluoroalkyl substances (PFASs), page 43*

on leachable material is arguably an overestimate. Therefore, we will assume a high case of 1ppm and a low case of 0.18 ppm, both well below the proposed limit of 50ppm for polymeric PFAS [15][16].

The actual quantities of FP waste entering the UK/EU landfill waste stream on an annual basis are estimated (Appendix 1) to be between 844kg and 1,316kg (best case scenario) and on 2,240kg and 3,334kg (worst-case scenario). These quantities in turn produce as little as 0.2g (best case) to as much as 3.3g (worse case) of leachable material.

Appendix 1:

Calculations of FPAS quantities entering landfill waste:

Two approaches have been adapted to estimate PFAS emissions released into the UK and EU environment as a result of disposal:

1. Annual quantities of PFAS materials consumed the industry (Table 1)

2. Annual sensor units sold (Table 3)

Number 0f sensors manufactured	**CO alarm sensors**	**Oxygen sensors**	**Toxic Gas sensors**	**Pellistors MO**	**NDIR PID**	**Gas Detectors**
UK +EU	8,100,000	2,900,000	6,550,000	1,263,000	505,000	101,900
ROW	19,200,000	500,000	2,500,000	700,000	220,000	453,000
TOTAL	**27,300,000**	**3,400,000**	**9,050,000**	**1,963,000**	**725,000**	**554,900**
ePTFE	**X**	**X**	**X**			
Dust Filter	**X**	**X**	**X**		**X**	**X**
PTFE powder	**X**	**X**	**X**			
Solid PTFE			**X**	**X**		
Fluoro-ether			**X**			
Tubing						**X**
Gasket						**X**

Table iii Annual number of sensors sold in the UK/EU and rest of the world (ROW) in 2022, their split into different sensor types (incl. CO alarm sensors, Oxygen sensors, Toxic gas sensors, Pellistors/MOx, NDIR/PID and Gas detectors), and the FP component parts i

Approach 1: Annual quantities of PFAS materials consumed

Values in Table 1 represent the total global used quantities. As we are only interested in quantities related to the UK/EU, we use the ratio of sensors sold in UK/EU to the global number of sensors sold according to Table 2 to estimate regional quantities. For example,

[16] *ibid, page 182*

$$ePTFE\ usage\ for\ CO\ sensors\ in\ UK|EU = Global\ ePTFE\ usage\ for\ CO\ sensors \times \frac{CO\ alarm\ sensors\ sold\ in\ UK|EU}{Total\ CO\ sensors\ sold\ globally}$$

$$= 3{,}443 \times \frac{11{,}100{,}000}{30{,}300{,}000} = 1{,}261\ (kg)$$

We also include gas sensor specific PFAS in this calculation. The relevant PFAS quantities are shown in Table 4.

	Gas sensor specific PFAS					General purpose fluoroplastics	
	ePTFE	**Dust filter**	**Solid PTFE**	**PTFE powder**	**Fluoro-ether grease**	**Gas tubing**	**Fluro-elastomer gasket**
TOTAL CO Sensors	1,022	129	0	12	0	0	0
TOTAL Gas Sensors	3,938	376	431	373	98	0	0
TOTAL Gas Detectors	0	59	23	0	19	1,115	1,178
GRAND TOTAL kg	**4,959**	**564**	**454**	**385**	**117**	**1,115**	**1,178**
SUMMARY kg	**8,773**						

Table iv PFAS materials usage in kg (UK and EU estimate based on percentage of total sensors sold)

In order to estimate the amount released to the environment (UK and EU only) due to disposal, we assume that PFAS emissions as a result of incineration and recycling are negligible, and only the materials that end up in landfills contribute to total emissions with estimated **1 ppm** emission. There are two scenarios considered here:

1. 15% of total disposed PFAS end up in landfill.
2. 38% of total disposed PFAS end up in landfill.

Estimated emissions for these two scenarios are calculated in Table 5 based on values from Table 4:

	Scenario 1	**Scenario 2**
Material disposed to Landfills	15%	38%
Gas sensor specific PFAS (Total kg - UK+EU) in Landfills	1,316	3,334
kg leach (based on 1ppm) WORST CASE based on all PFAS	0.001316	0.003334
kg leach (based on 1ppm) BEST CASE based on PTFE power only	0.000234	0.000592
Average WORST CASE = 3.3g, Average BEST CASE = 0.2g		

Table v Emissions (in kg PFAS) based on two disposal scenarios.

This calculation assumes that all PFAS has the same leaching potential (we call this WORST CASE), which we believe tends to overestimate actual emission values. The other assumption we made is that not all PFAS calculated in this way contribute to the emissions in the same manner. PTFE powder has a much higher potential to leach compared to solid ePTFE which accounts for all the other PTFE categories. Our BEST CASE only takes into account emissions from powder only, in the form of a percentage of the overall PTFE content in the sensor.

Approach 2. using the annual number of sensors sold

In order to estimate the total PFAS based on sensor sold, we need to know how much of the material is present for each sensor type in Table 2. Table 5 shows our best estimate of PFAS used in each material category for each sensor type. This allows us to calculate the total PFAS weight per sensor type.

	ePTFE	**PTFE powder**	**Solid PTFE**	**Grease**	**Dust filter**	**TOTAL (g) per sensor type**
Toxic sensor	0.1035	0.1500	0.1300	0.0500	0.0108	0.4443
Oxygen sensor	0.0500	0.0500			0.0045	0.1045
Domestic CO	0.0400	0.0600			0.0045	0.1045
NDIR/PID					0.0108	0.0108

Table vi PFAS (in grams) used in gas sensors per material category and sensor type.

For Gas Detectors, tubing and gaskets account for the majority of PFAS amount per unit. We estimated total PFAS per gas detector is about 18g, clearly a significantly higher content than for the small discrete sensor units.

We can then simply multiply the number of sensors sold by the weight of PFAS used in that sensor type. The result is shown in Table 7.

	CO alarm sensors	**Oxygen sensors**	**Toxic gas sensors**	**Pellistor/ MOx**	**NDIR/ PID**	**Gas Detectors**
Number of sensors sold in UK and EU	8,100,000	2,900,000	6,550,000	1,263,000	505,000	101,900
TOTAL kg PFAS	**846**	**303**	**2,910**	**0**	**5**	**1,830**
Summary kg TOTAL	**5,895**					

Table vii PFAS materials (in kg) used per sensor type.

We then follow the same logic used in Approach 1 to estimate the PFAS amount released to the environment (UK and EU only) due to disposal (Table 8).

	Scenario 1	Scenario 2
Material disposed to Landfills	15%	38%
Gas sensor specific PFAS (Total kg - UK+EU) in Landfills	884	2,240
kg leach (based on 1ppm) WORST CASE based on all PFAS	0.000884	0.002240
kg leach (based on 1ppm) BEST CASE based on PTFE power only	0.000157	0.000398
Average WORST CASE = 2.2g, Average BEST CASE = 0.2g		

Table viii Emissions (in kg PFAS) based on two disposal scenarios.

Note: proportion of average PTFE powder to total PFAS that is used for calculations of BEST CASE Leach is calculated based on values Table 6.

3. Emissions in the end-of-life phase:

Incineration:

Incomplete conversion of the FP parts to HF and CO_2 is the primary risk with incineration. It is argued[17,18] that if incineration treatment facilities use the correct temperature and residence times, complete conversion should occur; with appropriate scrubbing, no fluoride gaseous products should be present in the flue gases. Temperatures at the front end of an incinerator bed range from 900 – 1100°C[19], well above 800°C, the temperature concluded from a detailed literature study[20] by a Dutch national environmental and public health institute, for complete degradation of PTFE. Less stable FPs than PTFE such as PVDF, PFA, FEP should equally undergo complete degradation at 800°C. As mentioned in Section 2, this of course places the onus on the treatment centres to be rigorous in operating and maintaining their incinerators. Routine analysis of the incinerator exhausts as required to maintain their license would ensure compliance with the permissible PFAS emission levels being proposed.

Landfill:

The risk with landfill revolves around (i) the amount of leachable material, which in turn depends on the form (fine powders) and purity (presence of any residual PFAS polymerisation and processing aids) and (ii) bio-inertness or persistence. Fine powders have a high surface area and as interaction with the surrounding soil occurs only at the surface, fine powders have increased interaction. While the gas sensor/detector industry does indeed purchase fine powders, their form is changed to a sintered skeleton-type framework during the product manufacturing process to make electrodes for the sensor cells. The sintered form has a lower surface area, resulting in reduced leachable potential, reduced further by being encased in a sealed plastic pot. The risk of fine particulate matter entering the atmosphere is very low, due to the conversion of the particulate form to a sintered skeleton framework, and burying preventing weather erosion.

Regarding FP purity, the fluoropolymer industry in Europe[21] is committed to improving purity through minimising the use of non-polymer PFAS compounds. Section 2 discusses estimates of leachable material based on different scenarios, with concentrations well below the proposed threshold level of 50ppm for polymeric PFAS.

FPs satisfy very persistent (vP) criteria and will persist for decades if not centuries. With the present state of knowledge, there is no awareness of risks to the environment other than the < 1ppm of leached material and the build-up of landfill waste, i.e. persistence. The solution to arresting the build-up of stock is to reduce the volume of landfill waste, meaning moving towards a situation of 100% incineration.

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[17] Sales, J.; Hernández, F.; Kapoor, D; van den Noort, M; *Fluoropolymers: The Safe Science That Society Needs*-, International Chemical and Law Review, 2022

[18] Lohmann, R et al; *Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS?,* Environ. Sci. Technol. 2020, 54, 12820–12828

[19] A Asthana et al, *A 2-D mathematical model of on-grate munici- pal solid waste combustion* (2006) Sohn International Symposium Advanced Processing of Metals and Materials; A Asthana et al, 'A 2-D mathematical model of on-grate municipal solid waste combustion' (2006) Sohn International Symposium Advanced Processing of Metals and Materials.

[20] Rijksinstituut voor Volksgezondheid en Milieu, *Per- and polyfluo- rinated substances in waste incinerator flue gases* (2021).

[21] Plastics Europe, *Regulatory Management Option Analysis for Fluoropolymers* (2022) ***https://fluoropolymers.plasticseurope.org/index.php/fluoropolymers/irreplaceable-uses-1/reports-policy-documents/rmoa.pdf***

4. Impacts on the recycling industry:

Presently, recycling plays an insignificant part in the gas sensor/detector industry. Extracting the components from the discrete sensors for reuse is challenging due to tearing of the seals in those parts thermally sealed and corruption of other parts through contamination with Pb or electrolyte. Therefore, any recycling of the sensor parts would have to be directed to other uses following a cleansing step followed most likely by a milling step to convert them to powders. This would be an involved process and therefore cost effectiveness could be a determining issue here. Setting cost viability aside, the disposal of these powders would follow the scenarios described earlier in Section 2, generating emission levels which fall below the emission concentration threshold of 50ppm.

For gas detectors, the additional FP parts of tubing and gaskets parts (Section 2, Table 1- 4), are disposed through landfill rather than incineration based on CoGDEM members feedback, but there is no obvious impediment, apart from costs, to recycling these parts following a cleaning treatment into new gas sampling products. Costs would relate to collection and the cleansing treatments. Ultimately with repeat recycling, they would become unusable, but a successful recycling strategy would reduce the quantity of tubing and gaskets in circulation for gas sampling instruments. WEEE requires that tubing be disposed of correctly. Residual monomers are <50 ppb for ETFE, FEP and PFA, and < 1 ppm for PTFE with PTFE suppliers striving for even lower residuals[22]. Gas detector usage by CoGDEM members is 1115 kg/y for tubing and 1178 kg/y for gaskets based on sales into the UK/EU market (Section 2, Table 4)

For the third usage category of factory and laboratory test equipment (Section 2, Table 2), machined connectors have long lifetimes (>10 years) although the practice of recycling is low. Disposal is through WEEE controlled landfill or incineration, but the potential to cycle the UK/EU portion of the 1,318 kg/y used worldwide (Section 2, Tables 1-2) members is high as regeneration in a simple heat treatment to remove any built-up contaminants during service is possible.

Overall, there is no additional burden placed on the recycling sector because the FP materials highly pure with at most low ppm leachable discharges in water which will only improve in time based on commitments made by Plastics Europe, the trade body representing manufacturers[23].

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[22] B.J. Henry et al *A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers* Integr. Environ Assess Manag 2018:316–334 DOI: 10.1002/ieam.4035

[23] *"As such, all FPG Members have committed voluntarily to responsible manufacturing principles in term of continuously improve and/or develop best available techniques in the manufacturing process, management of environmental emissions, development of R&D programs for the advancement of technologies allowing for the replacement of PFAS-based polymerization aids, and/or the increase recyclability and reuse of its products in line with the objectives of circular economy."* PlasticsEurope's Fluoropolymers Product Group (FPG) statement, 2021.

5. Proposed derogations – Tonnage and emissions:

We are requesting an exemption rather than a derogation for ePTFE and powder PTFE used in the gas sensor/detector industry.

We are requesting a 12 year derogation for fluoro-elastomers, dust filters and fluoro-greases used in the gas sensor/detector industry.

Tonnage and emissions information has been provided in Section 2.

Tonnage:

The tonnage of FPs used per year was calculated from the cumulative responses of CoGDEM members to a detailed questionnaire. Based on quantities of FPs bought in, a value of 8.8 tonnes is estimated for 2022 (Section 2).

For purposes of corroboration, the tonnage estimate was also calculated by a different route. The same questionnaire provided information to enable determination of the number of sold sensors (Section 2, Table 3) for each different type (Toxic, Oxygen, CO, NDIR/PID). Knowing the weight of FPs in the different gas sensors (Section 2, Table 6), we were able to calculate the quantity of PFs in end-of-life sensors, i.e. going to disposal. The value resulting from this calculation was 5.9 tonnes, 67% of the 'FP quantities' figure. The discrepancy between the two figures is due primarily to stock retention in the gas detector segment and to a minor degree, manufacturing waste, which apart from one component, ePTFE, at 10% wastage due to membranes being stamped out of a sheet, is in the range of 0.5-6%.

Emissions:

According to Annex XV of the Restriction Report[24] *Plastics Europe* estimates 80% of fluoropolymer waste goes to incineration and only 15% to landfill, while European waste statistics for 2018 suggest landfill waste is as high as 38%. As we have two estimates of tonnage for waste disposal, 8.8 and 5.9 tonnes, we'll assume an average of 7.3 tonnes.

If incineration municipal treatment facilities apply the correct firing conditions with appropriate scrubbing, PFAS emissions are preventable[25], although further studies may be necessary for greater reassurance. Operation of treatment centres is a regulated activity and therefore it is assumed that operators will be rigorous in applying the proscribed firing protocols for optimum combustion of FPs.

Assuming incineration delivers FPAS emissions at the permissible levels, landfill is the primary source of waste emissions (recycling is too limited currently to be considered as an emission source). For the averaged 7.3 tonnes of FP waste, we have either 1.1 tonnes for 15% landfill or 2.8 tonnes for 38% landfill. Next, using the worst-case scenario of 1 ppm leachable material[26] and best case of 0.18ppm (see Section 2 for details), we arrive at the value range of 0.2 – 3.3 g of leachate going into the soil.

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[24] ECHA (2019b): Annex XV Restriction Report. Proposal for a Restriction: *ANNEX XV RESTRICTION REPORT – Per- and polyfluoroalkyl substances (PFASs), page 43*

[25] Sales, J.; Hernández, F.; Kapoor, D; van den Noort, M; *Fluoropolymers: The Safe Science That Society Needs*-, International Chemical and Law Review, 2022

[26] B.J. Henry et al *A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers* Integr. Environ Assess Manag 2018:316–334 DOI: 10.1002/ieam.4035

6. Missing uses – Analysis of alternatives and socio-economic analysis

7. Potential derogations marked for reconsideration – Analysis of alternatives and socio-economic analysis

8. Other identified uses – Analysis of alternatives and socio-economic analysis:

Fluoropolymers are critical components in gas sensors, but are not specified as a *sub-use* in the *Main applications* of ANNEX XV. See our comments to Information Request 1. For this reason, Information Requests 6. 7. and 8. Are combined in this report for Gas Sensors.

Gas sensors are often used in safety critical situations. Domestic carbon monoxide alarms save lives and the industrial safety related applications include gas monitoring in confined spaces for oxygen, combustible atmospheres and toxic gases; gas sensors mitigate risks to human safety and save lives.

In this section we first consider revenue from the gas sensor/ detector/ alarm industries, including the number of employees and customers.

This section then details alternative materials, their feasibility, timing and cost implications.

Gas Sensor/ Detector/ Alarm industries

As described earlier, this gas safety industry consists of three types of suppliers: industrial and CO gas sensors, gas detectors for industrial safety, and domestic CO alarms. Some detector manufacturers also manufacture sensors for use in their gas detectors. In this submission we are excluding medical gas monitors, gas analysers for laboratory and regulatory use and low cost consumer CO_2 monitors. Revenue generated from these three markets is detailed in the table below.

Revenue €	UK + EU	ROW	TOTAL	% UK + EU	% ROW
Industrial Safety Sensors	94,408,000	62,763,000	157,171,000	60	40
Domestic CO Alarms	70,705,000	185,000,000	255,705,000	28	72
Sensor and Detector Manu's	8,271,000	276,724,000	284,995,000	3	97
Detector Manufacturers	5,779,000	4,651,000	10,430,000	55	45
TOTAL €	**179,163,000**	**529,138,000**	**708,301,000**		

Table ix Revenue from gas sensors, industrial gas detectors and domestic CO alarms

Table 9 underestimates the EU income for sensor and detector manufacturers because on CoGDEM member, Dräger (Lubeck, Germany) is providing company information through the Figawa (Germany) Trade Association submission to ECHA. Total annual revenue for the EU+UK is greater than 200M€ if Dräger is included.

CoGDEM Employees	UK		EU		ROW	
	Manufacturing	**Other**	**Manufacturing**	**Other**	**Manufacturing**	**Other**
CO ALARMS	150	50	75	15		
GAS SENSORS	506	101	55	30	437	431
SENSORS + DETECTORS	30	85	28	43	577	995
GAS DETECTORS	62	0	0	0	90	60
GRAND TOTAL	**748**	**236**	**158**	**88**	**1104**	**1486**
REGIONAL TOTAL		**984**		**246**		**2590**

Table x Number of manufacturing and "Other" employees (includes sales, R&D and administration) for each supplier type

These companies employ just over 1,200 employees (plus Dräger and non-CoGDEM manufacturers), as shown in Table 10.

It is also revealing to understand the level of export beyond European borders; the table below lists the number of global customers in the EU, UK and ROW. We note that European manufacturers have about the same number of customers outside of Europe as inside Europe. Likewise, competitors in ROW already sell into Europe. This table excludes Domestic CO Alarm customers.

CoGDEM customers by Region	UK Manufacturing			EU Manufacturing			RoW Manufacturing		
	UK	**EU**	**ROW**	**UK**	**EU**	**ROW**	**UK**	**EU**	**ROW**
Gas Sensor Customers	322	713	824	30	75	75	77	212	205
TOTAL			**1859**	**180**			**494**		

Table xi customers by region. Excludes Domestic CO Alarm market: data was not available due to company confidentiality.

Alternative Materials: feasibility, timing and cost

The alternatives listed below are not drop-in substitutes for ePTFE, PTFE or other FPs. Each would need significant further development before it could be substituted for FPs in gas sensors. Ultimately, gas detection manufacturers rely upon their material suppliers for this development, but indications from the raw material suppliers are that replacements for these unique family of PFAS will be cost prohibitive and have timescales longer than the proposed maximum derogation period before replacement technologies become commercially available. Realistically, it is uncertain whether the FP alternatives known today will be capable of achieving equivalent technical performance while meeting the relevant regulatory standards. Therefore, replacing PTFE and other FPs in electrochemical gas sensors in a specified time frame is not feasible.

Note that we have focused our evaluation of ePTFE/fluoropolymers for use in both electrochemical gas sensor applications and as dust filters for all gas sensors. While some fluoropolymers are used in other gas sensor technologies, the large majority of fluoropolymer usage is in amperometric electrochemical gas sensors. A blanket prohibition on PFAS would require a similar evaluation of the components in other gas detection technologies: metal oxides, photo-ionization detectors (PIDs) and NDIR optical absorption for CO_2 and combustible gases.

Alternatives for ePTFE for gas porous substrates and solid barriers

Alternatives to PTFE and expanded PTFE (ePTFE) have been identified that can meet some but not all of the attributes required for gas porous substates and solid barriers.

Electrolyte leakage of gas porous (expanded) substrates can occur by seeping through microcracks that develop during use, especially during thermal cycling. This failure mechanism has been conquered with ePTFE and would require a very long time of material development and extended safety field trials for any alternative material to meet safety reliability requirements.

PTFE and similar fluoroplastics can withstand high processing temperatures. Electrochemical gas sensor electrodes require one, two or three elevated temperature stages, depending on the manufacturing method. These sintering/ bonding/sealing operations require temperatures in excess of 150°C, which either eliminates certain alternative materials or requires new sensor designs and electrode manufacturing operations that would already be used now if they were able to meet performance requirements. Developing new low temperature designs and processes for alternative materials will be a significant challenge.

Alternatives to Fluoroelastomers as gaskets, O-rings and sealants

Fluoroelastomers are used to seal components inside the gas sensor and in the gas sampling lines.

Alternative materials must resist oxidation and not react with acidic gases (ozone, nitrogen dioxide, chlorine, sulfur dioxide, hydrogen sulfide). Manufacturers of Digital Mass Flow Controllers (DMFCs) provide two grades of DMFCs for gas control: normal nitrile seals for most gases and Kalrez fluoroelastomer seals for reactive and acidic gases.

Manufacturers have not found a satisfactory alternative to expensive fluoroelastomers when using reactive or acidic gases, so likewise, replacing fluoroelastomers in gas sensor applications will be a technical challenge that to date has not been achieved.

Alternatives to Fluoroether greases

Specialist fluoropolymers can be found as greases inside of gas sensors because of their ability to withstand the extreme acidic conditions. These fluoro-greases also maintain the correct viscosity over the wide temperature range from -40°C to +60°C, a requirement that again will take time to provide a formulation with low viscosity-temperature dependence. Usage is very small- less than 250 kg per year.

Review of alternative materials

The alternatives listed below are not drop-in substitutes for PTFE or other FPs. Each would need significant further development before it could be substituted for PTFE in gas sensors.

Expanded Polypropylene (ePP)

- Expanded polypropylene membranes are hydrophobic, but with a higher surface energy than PTFE, limiting their use as gas porous substrates because of the potential to leak electrolyte.

- Unlike PTFE, ePP is not resistant to sulfuric or phosphoric acid, the standard electrolytes in electrochemical gas sensors. If they are manufactured as thicker substrates to improve lifetime in electrolytes, the gas diffusion and hence response time is too slow to provide a safe alarm.
- ePP lacks the thermal stability of FP; the melting point of polypropylene is 160°C versus 327°C for PTFE, so thermal processing during manufacture would require new developments.
- Mechanical performance is poor at low temperatures or after cyclic temperature exposures; this would need improving to avoid microcracks, leading to electrolyte leakage.
- While there may be the potential to improve the chemical resistance and possibly the thermal stability of expanded polypropylene via "surface cross-linking" this process may reduce the ability of this material to be recycled and introduce new problems within REACH. This approach has not been tested in sensors, so is a theoretical concept (TRL1) at this time.

Expanded Polyethylene ePE)

- With a melting point of only 120°C, expanded polyethylene lacks the thermal stability and processing temperature range required from an ePTFE replacement.
- ePE may offer relatively better electrolyte compatibility through improved acid resistance but is not as acid resistant as ePTFE..
- With a surface energy greater than ePTFE, ePE may leak electrolyte through the membrane, leading to the gas sensor failing unsafe (ie. it does not generate a signal when exposed to a toxic gas, so the gas detector decides that there is no gas present, which is unsafe).

Acrylic Copolymer

- The hydrophobicity and porosity of acrylic copolymer membranes are equivalent to that of PTFE and other fluoropolymers and have replaced FPs in some medical applications.
- The critical limitation is its chemical incompatibility with strong acids, which will limit its use with the electrolytes within electrochemical gas sensors.
- Limited processing temperature range means it is not suitable for replacement where elevated temperatures are required for sensor manufacture.

Polyether-ether-Ketone (PEEK)

- PEEK offers good temperature and chemical stability so it could be a suitable replacement in applications where there is direct, prolonged contact with corrosive electrolytes.
- The main limitation is the high surface energy, so it cannot be used as a gas porous substrate but could be used as an internal barrier.
- Not available as a liquid dispersion, limiting processing and manufacturing opportunities.

Polyurethanes (PU)

- Similar to PTFE, polyurethanes have both high thermal stability and hydrophobic behaviour.
- PU is not chemically compatible with strong acids, excluding it from internal sensor usage.

- Polyurethane will degrade is exposed to certain acid-type gases including hydrogen cyanide (HCN), hydrochloric acid (HCl), chlorine (Cl_2) and sulfur dioxide (SO_2), so cannot be as universal replacement for FPs.

Ceramics

- Some electrochemistry research has been published on ceramic membranes subjected to hydrophobic surface treatment, which offer good temperature and chemical stability.

However, this technology is not mature and has not yet been scaled up to commercial volumes.

- Ceramics are inherently brittle and rigid; their mechanical properties need improving to meet commercial gas sensor reliability requirements.

Estimates of time and cost for alternative Materials

CoGDEM members have estimated the time and cost for replacing FPs in gas sensors. Although estimates varied from optimistic to pessimistic, the accepted conclusion was that performance and reliability would be degraded with a significant cost to European gas sensor manufacturers at a time when the focus should be on zero carbon factories. Some CoGDEM members stated that there are no acceptable alternatives, especially for ePTFE. The tables below summarise CoGDEM members' estimates of time and cost for FP replacement.

Development Time	Minimum years	Median years	Maximum years
Particle filters	1	8	15
ePTFE electrodes	5	10	15
PTFE barriers	0.4	2	13.5
Machined/moulded fluoroplastics	0.75	1	15
Gaskets (fluoroelastomers)	0.75	7	13.5
O-rings (fluoroelastomers)	0.1	5	13.5
Fluoroether greases	5	7	13.5

Table xii Estimated research and development times for introducing alternative materials. Excludes CoGDEM members who stated that alternatives are not possible.

Development Cost	Minimum 1,000 €	Median 1,000 €	Maximum 1,000 €
Particle filters	**250**	**2,400**	**10,000**
ePTFE electrodes	**500**	**2,000**	**4,800**
PTFE barriers	**10**	**100**	**5,000**
Machined/moulded fluoroplastics	**100**	**150**	**800**
Gaskets (fluoroelastomers)	**150**	**500**	**800**
O-rings (fluoroelastomers)	**10**	**350**	**800**
Fluoroether greases	**300**	**550**	**800**

Table xiii Estimated development costs for introducing alternative materials. Excludes CoGDEM members who stated that alternatives are not possible. Costs are specific for each company.

Socio-economic Impact and Conclusions

It is clear that moving from fluoropolymer PFAS to alternative materials will have significant impact in the gas detection market, summarised below.

- There is no evidence that fluoropolymers are toxic.
- Emissions from manufacture and disposal are below REACH requirements and can be monitored and regulated.
- Fluoropolymer use in the gas detection industry (gas sensors, industrial gas detectors, domestic CO alarms) is a very small percentage of total European fluoropolymer usage (<10 t/y of the total 75,000 t/y usage).
- Fluoropolymers are critical components in gas sensors, especially amperometric gas sensors which are the universally accepted technology for industrial toxic gas detectors and domestic CO alarms. Alternative materials will not meet the performance and safety requirements. Fluoropolymers are expensive, so their use by all manufacturers underlines that there are no reasonable alternative materials.
- If fluoropolymers are banned in Europe, then manufacturers in ROW will increase their market share (approximately 50:50 between Europe and ROW) at the cost of a European market valued in excess of 200M€.

9. Degradation potential of specific PFAS sub-groups:

The FP materials, primarily PTFE and to a lesser extent PEPE (perfluoropolyether) are distinctly different classes of chemical compounds; they are not derivatives of the tri- and di- fluoromethoxy compounds.

10. Analytical methods:

Fluoropolymer (FP) emissions can be either:

- airborne as gases from incineration or particles from degradation
- in groundwater by monomer leachate or chemical breakdown

Unlike small molecule PFAS, specific FP emissions are not easily isolated. However, FPs used in gas sensors and gas detectors have a common chemical structure of a fully fluorinated backbone and high molecular weight and incineration and degradation products are common to the group of FPs used in gas sensors (PTFE, ETFE, FEP, PFA, fluoroelastomers).

To ensure consistency in measurements and uncertainty calculations, Test standards from national and international standards bodies should be followed. Although there is a paucity of CEN test standards for PFAS, ISO 21675 is recognised globally, with ASTM and EPA in the USA providing the majority of national test standards. The list below includes ISO and USA national test standards for sampling and analysing PFAS.

Water analysis

ISO 21675:2019 Water quality — Determination of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water — Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS)
EPA Method 537.1: Determination of Selected PFAS in Drinking Water by SPE LC/MS/MS
EPA Method 533: Determination of PFAS in Drinking Water by Isotope Dilution Anion Exchange SPE and LC/MS/MS
AWWA Technical Report 00039 Source Water Evaluation Guide for PFAS

Airborne analysis

ASTM WK81752 Standard Guide for Determination of Airborne PFAS in the Indoor Air Environment (in ballot stage)
EPA OTM-45 Measurement of Selected Per- and Polyfluorinated Alkyl Substances from Stationary Sources

Analytical methods

ASTM E3302-22 Standard Guide for PFAS Analytical Methods Selection
ASTM D8421 - Standard Test Method for Determination of Polyfluoroalkyl Substances (PFAS) in Aqueous Matrices by Cosolvation followed by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)
EPA Method 8327: PFAS Using External Standard Calibration and MRM LC/MS/MS

Quality standards for manufactured fluoropolymers

ASTM D6867-19 Standard Specification for Perfluoroalkoxy (PFA)-Fluoropolymer Tubing
ASTM D3307-21 Standard Specification for Perfluoroalkoxy (PFA) Resin Molding and Extrusion Materials

Quality management for PFAS waste

ASTM E3274-21 Standard Guide for Management of Investigation-Derived Waste Associated with PFAS.

11. List of Abbreviations and Tradenames

Abbreviations

BSI	British Standards Institute, the UK Standards Body
CEG	coal, electricity and gas industry
CENELEC	European Committee for Electrotechnical Standardisation
CO	Carbon monoxide
CoGDEM	Council for Gas Detection and Environmental Monitoring
ETFE	Ethylene Tetrafluoroethylene
ePTFE	Expanded PTFE, also termed gas porous PTFE when used for gas sensors
FEP	Fluorinated Ethylene propylene
HSE	UK Health and Safety Executive
IEC	International Electrotechnical Commission
ISO	International Standards Organisation
PFA	Per Fluoro Alkoxy Alkane
PFPE	Per Fluoro Poly Ether
PTFE	Polytetrafluoroethylene, the most common fluoroplastic with a very high melting point, excellent chemical resistance and very low surface energy
PVDF	Poly Vinylidene Fluoride

Trade names

Kalrez™	perfluroelastomer from Dupont
Viton™ FKM	Fluoropolymer made of Fluorine Kautschuk Material (FKM), sold by Chemours. Similar materials include Dai-El™ from Daikin, Dyneon™ from 3M, Technoflon™ from Solvay and Elaflor™ from HaloPolymer.
Fomblin™	Perfluoroether (PFPE) from Solvay. Other suppliers include DuPont Molykote™ and Castrol Braycoat™.
Fluon™	PTFE ETFE or PFA fluoropoplastic from AGC Chemical. There are many other global manufacturers of PTFE, ETFE or PFA.
Nafion™	Sulfonated tetrafluoroethylene, manufactured by Chemours.