

# Properties & production of labware from fluorinated hydrocarbons and their advantages for ultratrace analysis

by Joachim Dahmen, Klaus Englert and Gerhard Giebenhain  
(published in the 'International Laboratory - pacific rim edition -' in April/May 1997)

The smooth, inner surface of PFA labware combined with its hydrophobic and anti-adhesive properties opens new applications in ultratrace analysis. Very simple but effective acidic cleaning procedures can be applied, and good long-term stability of very diluted standard reference solutions in PFA labware allows the rationalisation of time-consuming sample preparation steps with improved results.

Today, the improvement in spectrometric methods for trace analysis has led to a change from the nano-(ppb) to pico-(ppt) mass range and, consequently, the demand made on the purity of chemicals for semiconductor processing has moved to the same range [1]. As a consequence, it is necessary to find suitable materials to enable ultra-clean sampling, sample preparation, sample analysis and storage of reagents, processing chemicals, analysis samples and reference materials. To achieve the expected high quality of analytical results, together with the adequate choice of instrumental technique e.g. ETV-AAS (electrothermal vaporisation atomic absorption spectrometry), ICP-OES (inductively coupled plasma optical emission spectroscopy) or ICP-MS (inductively coupled plasma mass spectrometry), know-how and high purity is required in all steps during the sampling and analysing process.

## Materials

Contamination of chemicals, samples and reference materials can be caused by:

- Interactions between the vessel material and chemicals (e.g. adsorption, desorption, leaching, diffusion, memory effects, etc.); and/or
- Bulk impurity of the vessel materials used during the analysing process, resulting from production processes.

When polyolefinic materials like polyethylene (PE) or polypropylene (PP) (see table 1) are used, problems are encountered due to the use of Ziegler-Natta or Philipps catalysts (especially Al, Cr, Mg, Si, Ti or Zn) in the production process of the polymers, which leads to contamination and unacceptable concentration changes of low concentration samples over periods as short as 24 hrs [2].

Additional problems can be caused by leaching of other elements (Fe, Hf, Li, Mo, Na, Nb, Ni, Ru, Ta, V, W and Zr, and, less often, Os, Pd, Re, Th and U) from the catalyst [3].

In contrast, the fluoropolymer PFA is manufactured without any catalyst which could cause contamination. As a consequence, it is highly preferable to use fluoropolymer materials when working in the lower  $\mu\text{g/g}$  (ppm),  $\text{ng/g}$  (ppb) or  $\text{pg/g}$  (ppt) ranges.

Fluoropolymers possess quite extraordinary properties (see table 1). Their high thermal stability and their unsurpassed chemical resistance are caused by the extremely stable valency bonds between C

and F atoms and the helical F structure which successfully protects the linear C chain of these fluoropolymers (fig. 1). In addition, they have accentuated hydrophobic and anti-adhesive properties. und Geochemie der TU Karlsruhe für die Durchführung der Messungen.

PTFE (Polytetrafluoroethylene) is the most widely known fluoropolymer, with PTFE labware being used in many laboratories. High thermal stability (from -200 to +260°C) and high chemical resistance against almost all chemicals are the most important advantages of this material.

However there are disadvantages too, especially when working in ultratrace analysis, due primarily to the fact that formation of PTFE is only possible by isostatic pressing, sintering and machining. In the isostatic moulding process, PTFE is placed in a mould which is then compressed into a 'pressed billet', which has a sufficient strength to be handled. These PTFE billets are finally heat sintered. The result is a kind of microporosity in the material, while the final machining also causes the product to have rather rough surfaces (fig. 2).

PFA is a recently developed derivative copolymer of PTFE and is a very pure material, polymerized without any leachable additives. In contrast to the opaque PTFE products, PFA has a good transparency. Using modern manufacturing techniques like injection-moulding and blow-moulding, it is possible to manufacture PFA products with ultra-smooth inner surfaces.

## Surface Characterisation



Fig. 1  
SEM image of surface of a PTFE beaker (left) and a PFA evaporating dish (right). REM x8000, sample tilt 30°.

An important aspect in choosing the most suitable vessel material in ultratrace analysis is the knowledge of its surface properties. Therefore, a fundamental study of the surface topography and of the influence of production parameters like moulding temperatures in the production of PFA labware was performed [4].

Characterisation of surface topography requires the use of various different analytical approaches. For example, scanning electron microscopy (SEM) can be used for qualitative reproduction of the surface morphology, whereas profilometry and atomic force microscopy (AFM) can be used for the

quantitation of surface roughness. A thorough characterisation of different fluoropolymers was performed [4]. The results of this characterisation should be helpful for the proper choice of suitable material for labware and processing and handling facilities and tools. The results of the study may be summarised as follows:

PTFE labware (fig. 1a) exhibits a very rough surface with many deep pores and material inhomogeneties and protrusions on the surface. PFA labware (fig. 1b) shows an extremely smooth surface with lowest surface roughness.

The quality of the surface generally depends on many production process parameters. In particular, the temperature during the production is decisive for the surface quality. Using modern manufacturing techniques (injection moulding and blow moulding), it is possible to manufacture PFA labware with ultrasmooth inner surfaces. Because of the extreme hydrophobic and antiadhesive properties of PFA, it is possible to use quick and simple acidic cleaning procedures (fig. 3) when preparing this labware for trace analytical purposes [5]. Conventional quartz vessels being prepared for trace analysis require considerably longer, more powerful and more costly cleaning methods (e.g. boiling or steaming for many hours with nitric acid) [6].

### Investigations on leaching & cleaning of PFA labware [7]

The accuracy of the results in trace analysis can be affected by the purity of labware used to hold the sample. To determine the purity of new uncleaned bottles (250, 500 and 1000 ml) made from PFA, two specimens of each volume were filled with 50 g of fresh sub-boiled 65% HNO<sub>3</sub>. After 4 hr, the concentration of trace elements leached by the acid was determined with ICP-MS. The results are shown in Table 2. In the second test the same bottles were filled again with 50 g of HNO<sub>3</sub> (65%), shaken and stored for 6 days at 20°C. The result of the analysis showed that all elements were below the level of detection of the method (LOD < 0,1 ng/ml). From this determination, it can be concluded that:

- New uncleaned vessels contain a range of trace elements which may be leachable into the chemical, samples and reference materials filled into the bottles. This makes the cleaning of vessels necessary before filling.
- There is a correlation between leached amounts of trace elements and the dimension of the inner surface of the vessels; namely the larger the inner surface, the higher the amount of leached traces.
- Acidic cleaning of PFA vessels is simple, and results in a reliable reduction of the danger of contamination. This is one of the most important advantages of PFA labware (see figures 4 and 5).

### Conclusion

PFA is particularly suitable for the manufacture of labware to be used for ultratrace analysis. Using modern manufacturing processes together with optimised production parameters, a very smooth inner surface of the final product is obtained. Due to the surface properties, together with the extreme temperature and chemical resistance, labware made from PFA can help to increase the quality of results in ultratrace analysis. Simple and easy cleaning procedures and the long stability of

chemicals and reference materials in PFA labware help to improve the accuracy of results in analytical laboratories and hence their economical performance.

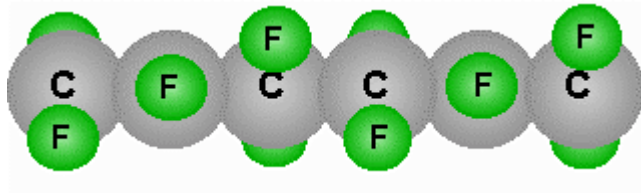
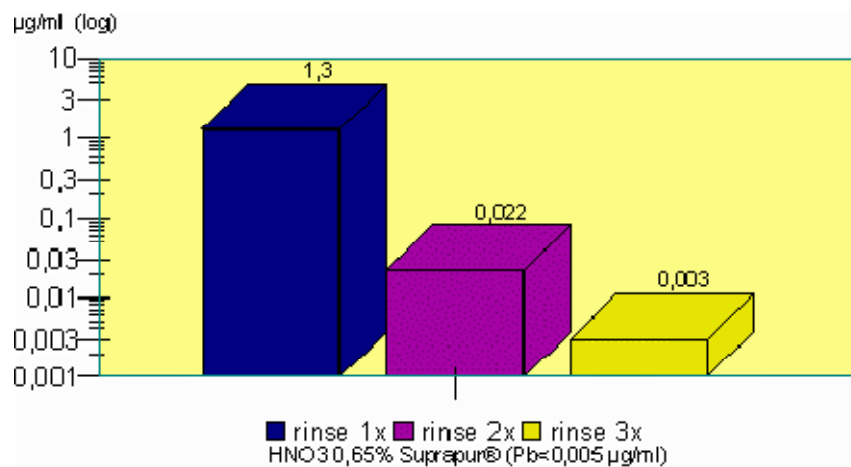


Fig. 2  
Stretched fluorocarbon polymer chain, showing the protection of C backbone by the helical F outer structure.



Cleaning of highly contaminated PFA volumetric flasks.

After pre-rinsing with nitric acid, PFA volumetric flasks (500 ml) were contaminated with 200 ml of Pb standard reference material (Pb c=1 mg/ml).

After this, the flasks were rinsed 3 times with 50 ml of 0.65% nitric acid (Suprapur®) (Pb<0.005µg/ml).

After each rinse, Pb was determined by ICP-AES. Subsequently, the volumetric flasks were completely filled with Suprapur nitric acid and allowed to stand for 6 days. Afterward, the acid was tested again. There was no measurable increase in Pb.

It can be concluded that it is possible to clean PFA labware easily and quickly by repeated rinsing with cold, clean nitric acid [5].

**13 elements: Al, B, Cd, Co, Cr, Cu, Li, Mg, Mn, Ni, Sr, Zn.**  
**Methode: ICP-MS (Total-Quant).**

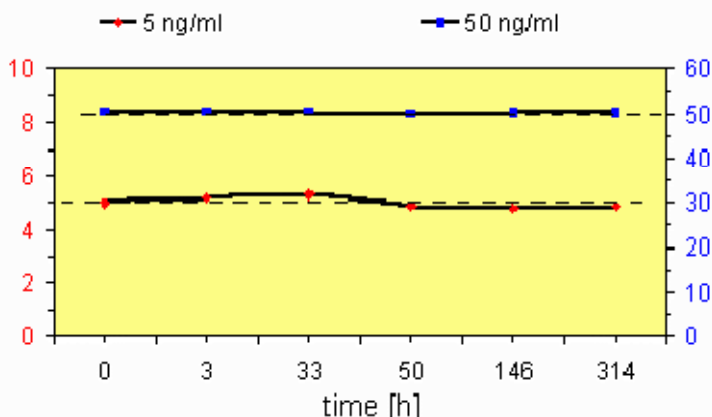


Fig. 4

Stability of highly diluted multielement reference standards: Ag, Al, B, Cd, Co, Cu, Li, Mg, Mn, Ni, Sr, and Zn. Solutions were diluted to 5 and 50 ng/ml in PFA flasks. Determination was performed by ICP-MS. [2]

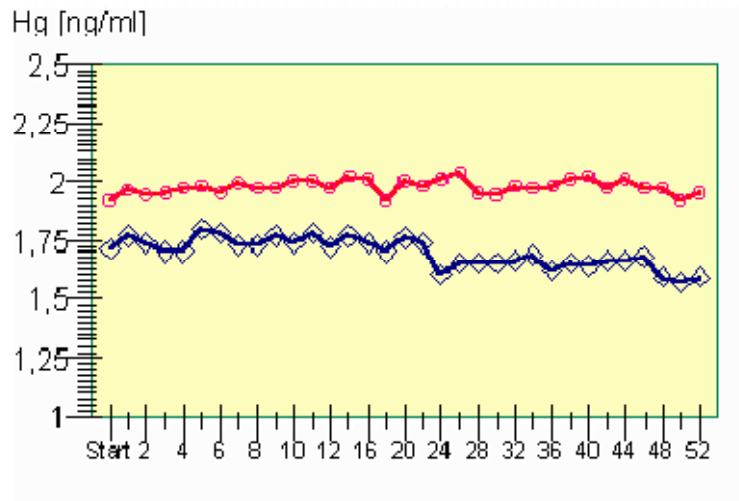


Fig. 5

Stability of Hg reference solutions diluted to 2 ng/ml both with and without stabilisation by dichromate (DEV E12). Determination by cold vapour AAS. [8]

Table 1

### Properties of different materials for labware for trace analysis

	SiO <sub>2</sub>	PE	PP	PTFE	PFA
<b>Name</b>	Quartz	Polyethylene	Polypropylene	Polytetrafluoroethylene	Perfluoroalkoxy
<b>Permeability</b>	Low	Low	Medium	Medium	Low
<b>Temperature from °C</b>	-10	-50	-10	-200	-200
<b>to °C</b>	+1000	+80	+130	+260	+260
<b>Manufacture <sup>a</sup></b>	BM	BM/IM	BM/IM	Sinter	BM/IM
<b>Chemical Purity <sup>b</sup></b>	<µg/g	<µg/g	<µg/g	>µg/g	<< ng/g
<b>Structure</b>	SiO <sub>2</sub>	-[CH <sub>2</sub> CH <sub>2</sub> ] <sub>n</sub> -	-[CH <sub>2</sub> C(CH <sub>3</sub> )H] <sub>n</sub> -	-[CF <sub>2</sub> -CF <sub>2</sub> ] <sub>n</sub> -	-CF <sub>2</sub> CF <sub>2</sub> C(OR)FCF <sub>2</sub> CF <sub>2</sub> ] <sub>n</sub> - (R=C <sub>n</sub> F <sub>2n+1</sub> )

<sup>a</sup>BM, blow moulding; IM, injection moulding, Sinter, isostatic moulding.

<sup>b</sup>Maximum leachable amount of contaminants.

Table 2

**Results of investigations of the leachability of trace elements from new PFA labware bottles after 4 hr (A) and 6 days (B).[7\*]**

Bottle	1000 ml		500 ml		250 ml	
	A	B	A	B	A	B
Al	1.0	6.3	2.0	0.8	0.8	0.8
Ca	2.0	15.0	6.0	3.0	2.4	4.0
Fe	1.0	7.0	4.0	11.0	2.0	3.2
K	0.9	5.0	2.0	1.0	0.8	1.2
Mg	0.3	2.0	0.8	0.4	0.4	0.4
Na	0.8	5.0	2.0	1.4	2.4	2.8

\* Concentration (ng per bottle volume) of leachable trace elements recalculated in relation to the filling volume (100 %) of the bottle investigated. The table indicates possible contamination when dispensing highpurity acids into new, uncleaned bottles. (Reproduced with permission from Ref. 7.)

**Authors:**

Dr Dahmen is Ultratrace Analyses Project Manager, Central Services Analyses, Germany

Mr Englert is Marketing Director, Germany

Dr. Giebenhain is a Chemist, Germany

The authors wish to thank the Central Services Analyses of **Merck KGaA** for their support, and T. Rest and co-workers, Kaliforschungs-Institut, **Kali und Salz AG**, Heringen, Germany; N. Müller and co-workers, **Hoechst AG**, Frankfurt, Germany; and H. Punchelt and co-workers, Institut für Petrografie und Geochemie, TU Karlsruhe, Germany; for their assistance and investigations. This article is based on a paper presented at the 4rth Russian-German-Ukranian Analytical Symposium, Sofrino, Moscow, Russia, February 25 - March 3, 1996.

**References:**

- [1] SIA-The National Technology Roadmap for Semiconductors. San Jose, CA, 1994.
- [2] Giebenhain G. Rath HJ. GIT Fachz. Lab 1995:247-50.
- [3] Reddy SS, Sivaram S. Prog Polym Sci 20:309-67.
- [4] Xu HH, Ortner HM, Dahmen J., Opfermann H, Englert K, Gortz W. Surface characterisation of fluorinated polymers (PTFE, PVDF, PFA) for use in ultratrace analysis. Fres J. Anal Chem 1996; 355:657-64.
- Poster session XXIX Colloquium Spectroscopicum Internationale, Post Symposium ICP-MS and 11th German ICP-MS Users 'Meeting', Wernigerode, Germany 1995; Fres J Anal Chem, in press.
- [5] Englert K, Giebenhain G, Mosch H-J, Müller N. GIT Fachz Lab 1997; 32.
- [6] Tschöpel P, Kotz L, Schulz S, Veber M, and Tolg G. J Anal Chem 1980; 302:1-14.
- [7] Büttner W, Dahmen J, Harder N, Heckenkamp J. GIT Fachz Lab 1993; 992-96.

The figures quoted are recommendations, we do not assume any liability for their correctness !