# New filter rating method in practice for sub 30 nm lithography process filter

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## ABSTRACT

A new method for rating retention in lithography process filters has been developed. The method employs a gold nanoparticle contaminant challenge, inductively coupled plasma mass spectrometry as a concentration detector, and dynamic light scattering as a particle size detector, all of which enable accurate, reliable filter retention rating below 30 nm. There is good agreement between results obtained with the new method and results obtained with a conventional polystyrene latex bead challenge. A filter that was rated at 10 nm using extrapolative methods was confirmed to be 10 nm using the new challenge test. Microbridge removal efficiency of polyethylene filters rated by the new method was studied in a 193 nm (dry) lithography process and the new method was verified. When applied to commercially available filters that are rated below 30 nm, the new method revealed significant differences in removal efficiency among similarly labeled filters.

**Keywords:** Filtration, rating method, gold nanoparticle, lithography

## 1. INTRODUCTION

As the minimum acceptable defect size continuously shrinks with lithographic patterning dimensions, greater demands are placed on the retention capabilities of process fluid filters.[1] For finer filter development and its application to the lithography process, the establishment of an accurate retention rating method is a key step. However, such a method has not been available for recent litho technology nodes, due to limitations in suitable particle challenge material and detectors.

Polystyrene latex (PSL) beads have been widely used as the standard challenge particle in rating liquid filtration products for over 20 years. However, production of a sub-20 nm PSL bead has been difficult. Also, traditional particle-counting technology has reached a limitation for detecting and counting particles smaller than 30 nm. Several years ago, fluorescent PSL (f-PSL) spheres were developed applied as a filter rating method by using a fluorescence spectrophotometer in order to realize improved detection sensitivity compared to traditional particle counters. However, f-PSL shares the same particle size limitation as conventional PSL spheres. Furthermore, some studies show that fluorescent or dye material fixed to the PSL sphere surface is easily dissolved or released into liquid phase because of poor weathering durability.[2] Disassociation of fluorescent material from the challenge particle can lead to difficulty in accurately measuring the challenge particle concentration, and ultimately, an overestimation of particle removal efficiency. Traditional retention rating methods used for ultra-filtration (UF) products employ different challenge materials (more biologically-based, like proteins, viruses, and biopolymers) and a different rating metric (MWCO – molecular weight cutoff). However, micro-filtration (MF) membranes have been historically rated with “hard” sphere particles, in order to maximize measurement reliability—that is, to minimize variation due to challenge particle aggregation, deformation, and dimensional distribution (e.g., shape, aspect ratio). Thus, it is reasonable to continue adhering to the fundamentals of traditional MF rating methods.

The work to follow describes a new method developed by Pall Corporation for rating sub-30 nm filters in process liquids. The method employs several novel applications of well-defined materials and analytical techniques, including gold nanoparticles as a challenge material, inductively coupled plasma mass spectrometry (ICP-MS) as a concentration detector, and dynamic light scattering (DLS) as a particle size detector.[3] The method developed was applied to several commercially available lithography process filters that are rated at 30 nm and smaller. Also, retention ratings are supported using process defect data.

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### 1.1 Current filter rating methods

A filter's retention rating is defined as the minimum size of particle that the filter is able to remove with a certain degree of efficiency. Currently, filter retention rating is determined using a method that measures removal efficiency of a standard PSL bead particle challenge. A liquid particle counter (LPC) is used to measure both particle size and particle concentration. This method has limitations due to the minimum particle size available, which is greater than 20 nm, and the minimum detectable particle size for LPC equipment, which is 30 nm.

Given these limitations, alternative methods have been used to estimate filter retention ratings below 30 nm. One typical method is extrapolation using the inverse linear relationship between knee location (KL) value and membrane pore size. KL is the critical pressure at which the liquid film of a standard wetting agent, such as isopropyl alcohol, that is formed to membrane pores bursts (i.e., the bubble point). Theoretically, KL is inversely proportional to the membrane's median pore diameter, as shown in equation (1). An illustration of this extrapolative method is shown in Figure 1.

$$D = \frac{S\gamma \cos\theta}{KL} \qquad (1)$$

where: KL = knee location (critical pressure)

S = coefficient related to media structure

$\gamma$ = the surface tension of the liquid

$\theta$ = liquid-solid contact angle

D = pore diameter

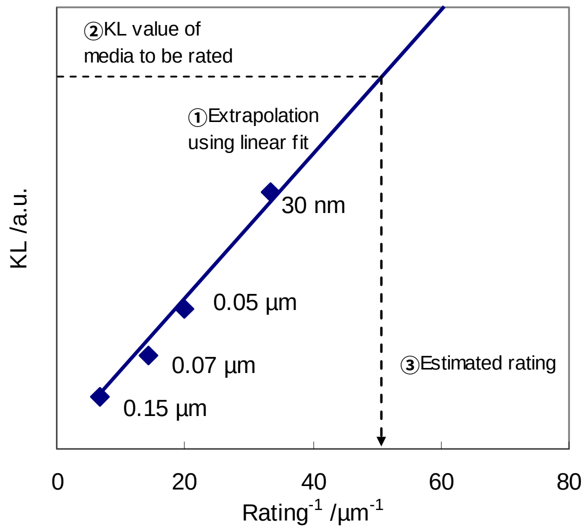


Figure 1. Illustration of retention rating below 30 nm using KL value extrapolation. Rating from 0.15 µm to 30 nm were determined by PSL-LPC challenge test.

As the KL-Rating relationship is dependent on media structure (S, in equation (1)), extrapolation results are only valid for membrane media of similar structure. Another alternative rating method is to compare standard PSL-LPC challenge test results and extrapolate based on the removal efficiency of challenge particles that are larger than the proposed rating. A filter that demonstrates greater removal efficiency for a given particle size is estimated to have a finer removal rating.

The aforementioned retention rating methods do have limitations and do not directly measure the retention of particles smaller than 30 nm. As advances are made in the lithographic patterning process and critical defect size continues to decrease, there is an increasing need to measure sub-30 nm particle retention directly. The newly developed rating

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method can be used to validate extrapolative (indirect) rating methods and is useful in the development of finer filter membranes.

### 1.2 Gold nanoparticle challenge test

Table 1 lists several methods for rating filters below 30 nm. As a result of detailed study, especially focusing on particle size precision and stability, and detection system accuracy and reliability, Pall Corporation selected a method that employs gold nanoparticles as a challenge material, ICP-MS as a concentration detector, and DLS as a particle size determination.[3] Gold nanoparticles provides several advantages such as:

1. NIST (National Institute of Standards and Technology) classification as a standard reference material
2. A wide range of commercially available sizes (30 nm to 2 nm)
3. Inert chemical nature, which ensures stability during testing and minimal environmental contamination due to testing.

Table 1. List of standard particles and corresponding detection methods

| **Particle** | **Type** | **Available particle sizes (<30 nm) [nm]** | **Detector (Size)** | **Detector (Count or Conc.)** | **Relative detection sensitivity** |
|---|---|---|---|---|---|
| Gold nanoparticle | Hard | 2, 5, 10, 15, 20, 30 | DLS | ICP-MS | High |
| PSL | Hard | 21, 33* | LPC | LPC | Low to Medium |
| Fluorescent PSL | Hard | 20, 30 | Not established | Fluorescence Spectrophotometer | Medium |
| Colloidal silica (includes $CeO_2$, $TiO_2$) | Hard | 5, 10, 20, 30 | Not established | NRM | High |
| Bacteria | Soft | Not determined | Not established | Culture | Medium |
| UF rating material (Protein, Virus, etc.) | Soft | 1.1 – 8.4 (estimated) (MW 340 – 150,000) | GPC | UV-Vis | Low |

DLS: Dynamic Light Scattering, also called Photon Correlation Spectroscopy (PCS)
ICP-MS: Inductively Coupled Plasma Mass Spectrometer
PSL: Polystyrene Latex
LPC: Liquid Particle Counter
NRM: Non-volatile Residue Monitor
GPC: Gel Permeation Chromatography
UF: Ultra-filtration
MW: Molecular Weight
UV-Vis: Ultraviolet-Visible Spectrophotometer

*: 3000 series Nanosphere™ (Thermo Fisher Scientific, US)

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## 2. EXPERIMENTAL

### 2.1 Gold nanoparticles

Figure 2 shows in-lens field emission scanning electron microscopy (in-lens FE-SEM) images of the gold nanoparticles.[3] Gold nanoparticles (EMGC series, 5, 10, 15, 20, and 30 nm), supplied by British Biocell International, UK, were suspended in dilutions of deionized water at a concentration of 0.5 ppm. In order to minimize particle retention via other mechanisms (e.g., electrostatic adsorption), an appropriate protective ligand was added to the gold nanoparticle suspension. A similar treatment (Triton-X) is used in the conventional PSL-LPC rating method,[4] in order to encourage classical hard sphere interactions from the challenge particles. Based on results from a previous study[3], mercaptosuccinic acid and 2-amino-2-hydroxymethyl-1,3-propanediol were selected as protective ligands while evaluating polyethylene and nylon 6,6 filtration media, respectively. Mercaptosuccinic acid was introduced at concentrations of 0.5 mmol/L for 5 nm particles, and 0.1 mmol/L for 10 nm and 30 nm particles. 2-amino-2-hydroxymethyl-1,3-propanediol was prepared at a concentration of 0.1 mmol/L.

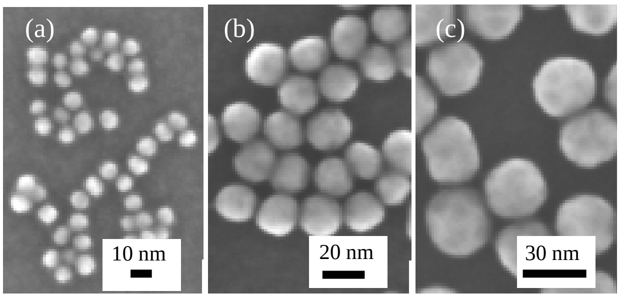


Figure 2 In-lens FE-SEM images of gold nanoparticles. (a) 10 nm, (b) 20 nm, (c) 30 nm.

### 2.2 Filter media

Two types of membrane media that are typically used in the lithography process were evaluated: Polyethylene, which possesses a non-polar chemical bond distribution, and nylon 6,6, which contains polar peptide moieties that help to enable an adsorptive retention mechanism. Polyethylene media tested were from Pall PE-Kleen™ filters rated at 30 nm and 10 nm. The 30 nm PE-Kleen filter rating was determined by conventional PSL-LPC method, whereas the 10 nm PE-Kleen filter rating was presumed based on both KL extrapolation method and superior retention efficiency of 33 nm PSL spheres vs. the 30 nm PE-Kleen filter. Nylon 6,6 media tested was from a Pall Ultipleat® Asymmetric P-Nylon filter rated at 20 nm. The 20 nm Asymmetric P-Nylon filter rating was determined using 21 nm PSL beads as a challenge particle and a UV spectrometer to detect particle concentration. Further, commercially available polyethylene media filters, labeled as 5 nm and 10 nm, were also evaluated.

### 2.3 Gold nanoparticle challenge test

The particle challenge test was conducted using the test stand shown in Figure 3. Test fluid (gold nanoparticle suspension) was supplied to the filter media (47-mm disk) using air pressure that was controlled to maintain a constant flow rate of 5 mL/min. The initial 10 mL of effluent was discarded in order to avoid possible contamination that may accompany the transition from stagnation to flow. The subsequent 10 mL of effluent was collected for measurement. Each test was repeated twice to check repeatability.

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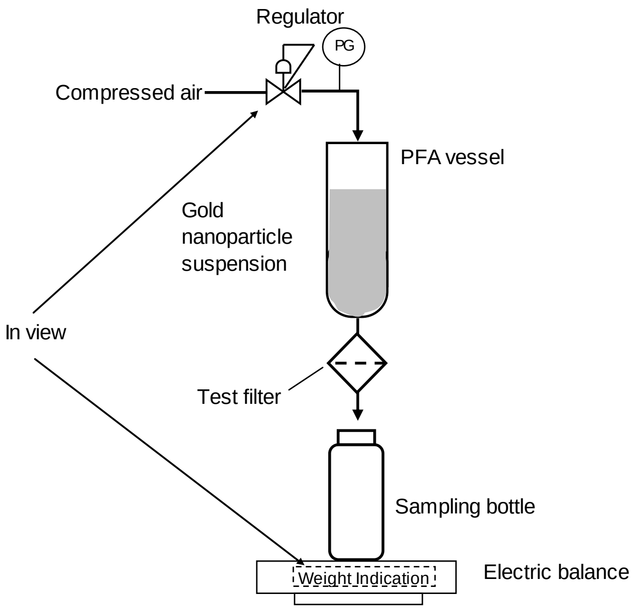


Figure 3. Test stand employed for gold nanoparticle challenge test. Constant flow rate is maintained by controlling upstream air pressure.

### 2.4 Measurement

Elemental gold concentrations in the influent and the effluent were determined using ICP-MS (HP-4500, Agilent Technologies, US). The measurement was conducted with shield torch normal plasma. A calibration curve was generated using dilutions of a standard solution ($HAuCl_4$, Wako, Japan) in the range of 0 to 500 ppb. Removal efficiency was calculated using measured gold concentrations; the mean value of three measurements is reported. To confirm particle size distribution in the challenging test, both DLS (Zetasizer® nano ZS, Malvern, UK) and electron microscopy were used. Specifically, transmission electron microscopy (TEM) observation was conducted for 5, 10, and 20 nm particles, and in-lens FE-SEM observation was used to verify 30 nm particles.

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## 3. RESULTS AND DISCUSSION

### 3.1 Gold nanoparticle challenge test for lithography process filters

#### 3.1.1 Particle size distribution

Figure 4 shows particle size distributions for 5, 10, 20 and 30 nm gold nanoparticles, as measured by TEM and in-lens FE-SEM observation. Measurements confirm that median particle sizes were consistent with the respective labels, and possessed low degrees of polydispersity. As reported previously, DLS measurements of both influent and effluent confirmed the absence of nanoparticle aggregation.[3]

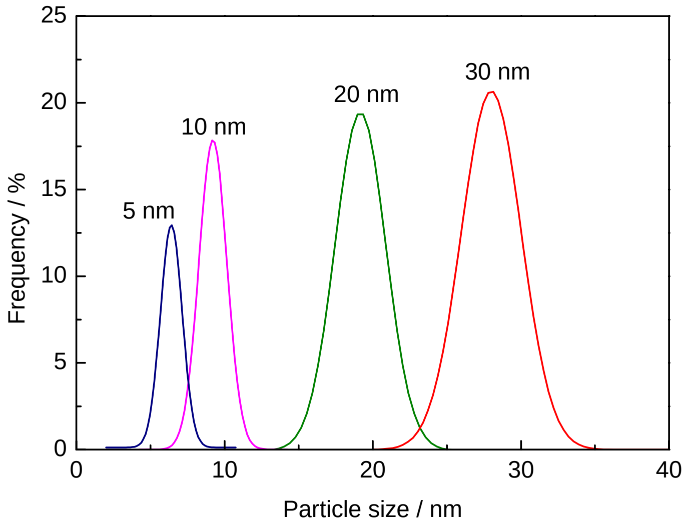


Figure 4. Particle size distribution (PSD) for 5, 10, 20 and 30 nm gold nanoparticles. PSD determined by observation of TEM for 5, 10, 20 nm and in-lens FE-SEM for 30 nm.

#### 3.1.2. Removal performance for lithography process filters

Results of gold nanoparticle challenge test for the advanced lithography process filters are shown in Figure 5. The 30 nm PE-Kleen filter showed 99% of removal efficiency of 30 nm gold nanoparticles. The 20 nm Asymmetric P-Nylon filter showed 99% removal efficiency of both 30 nm and 20 nm gold nanoparticles. The removal efficiency of each filter was observed to decrease for gold nanoparticles that were smaller than respective removal ratings. Moreover, the 10 nm PE-Kleen filter showed 99% removal efficiency of 10 nm gold nanoparticles, and showed a similar decrease in removal efficiency against smaller particles (5 nm). Thus, results indicate that, for 30 nm PE-Kleen, 20 nm Asymmetric P-Nylon, and 10 nm PE-Kleen filters, there is good agreement between the new filter rating method and the conventional methods that were originally used to rate these products.

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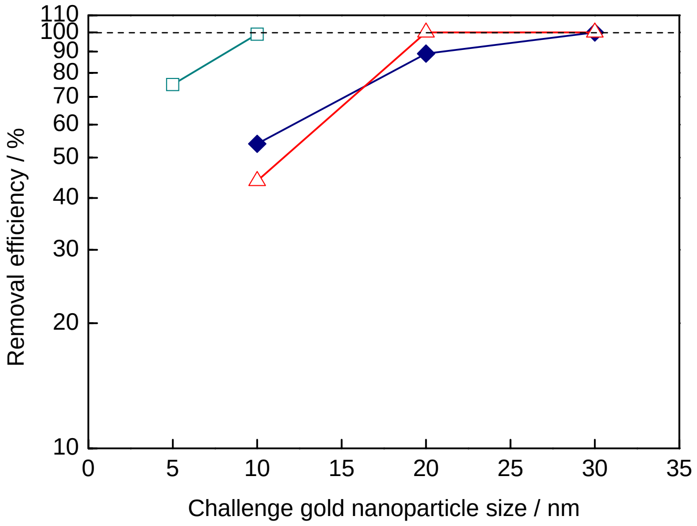


Figure 5. Removal efficiency measured by gold nanoparticle challenge test in water for various lithography filters, ◆: 30 nm filter ("PE-Kleen", Pall ), △: 20 nm filter ("Ultipleat Asymmetric P-Nylon", Pall), □: 10 nm filter ("PE-Kleen", Pall).

### 3.2 Validation of gold nanoparticle challenge test in field test

In previous studies, the effect of polar bond groups in filter media material for reducing microbridge defects was made clear .[5,6] That is, in filtration with nylon 6,6 media, electrostatic adsorption of certain defect precursors is achieved by polar amide functional groups, whereas mechanical sieving is the primary retention mechanism for non-polar polyethylene media. Figure 6 shows microbridge defect removal data that were previously reported for PE-Kleen and Asymmetric P-Nylon point-of-use filters within a 193 nm dry lithography process.[5] For nylon 6,6 membrane filter, better microbridge reduction than 10 nm polyethylene membrane filter was observed. This disagreement with the rating result was due to difference of the filtration mechanism in field evaluation and in filter rating. That is, filtration using nylon 6,6 media includes adsorptive effect, and high removal efficiency is achieved in point of use filtration. On the contrary, filter rating in PSL-LPC and gold nanoparticle challenge test is, as mentioned above, conducted under no adsorptive effect. For polyethylene membrane filters, results suggest a relationship between filter retention rating and microbridge defect reduction, with the finer filters showing a greater extent of defect removal. In this case, sieving is the dominant mechanism for both point of use filtration and gold nanoparticle challenge test. Thus, filter ratings based upon the gold nanoparticle retention test can be used confidently as a guide for selecting a filtration product that provides required performance for lithography processes.

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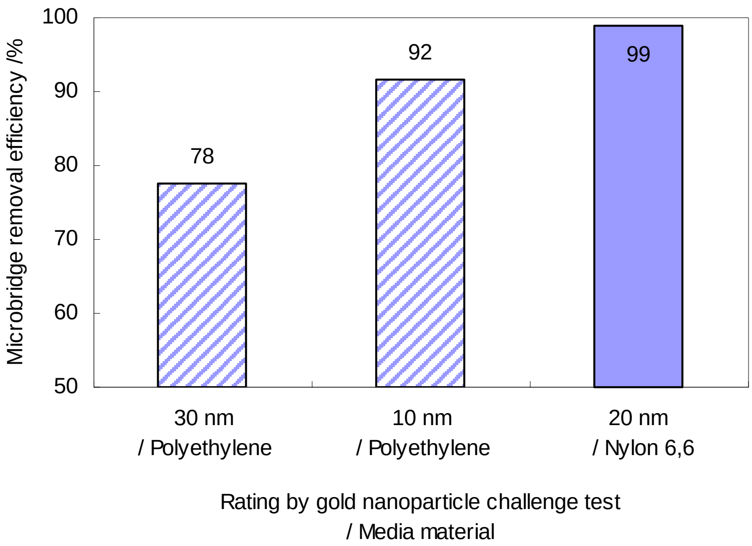


Figure 6. Microbridge removal efficiency as a function of gold nanoparticle rating.

### 3.3 Gold nanoparticle removal performance for commercially available filters rated below 30 nm

Figure 7 shows gold nanoparticle challenge test results for several commercially available filters that are rated below 30 nm. The media material for all test filters is polyethylene. Figure 7a shows the results for filters labeled as having a "5 nm" retention rating, as well as for two Pall polyethylene media samples that are candidates for a retention rating of 5 nm. Results show that there is a significant difference between commercially available filters A and B, with removal efficiencies around 70%, and the two Pall media candidates, which each show greater than 90% removal efficiency.

Similarly, Figure 7b shows comparative results for filters labeled "10 nm". Again, there is significant disparity between two different filters that carry the same retention rating. In agreement with previous results on flat sheet membrane (Figure 5), the Pall 10 nm PE-Kleen filter demonstrates 99% removal efficiency of 10 nm gold nanoparticles, while Filter C shows less than 50% removal efficiency.

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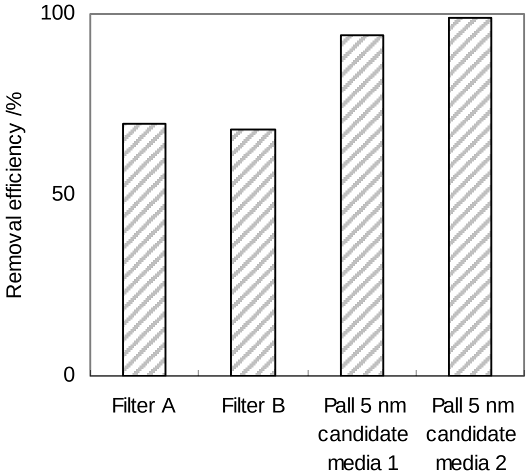
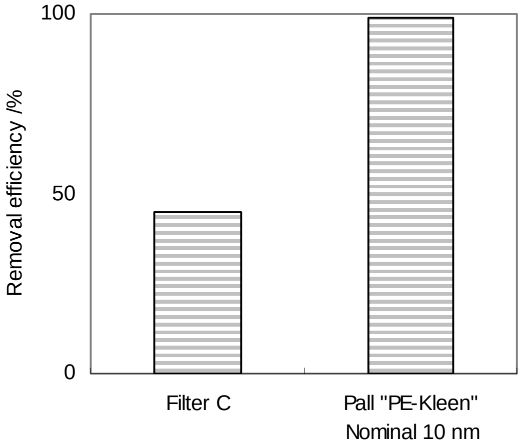



(a) Filters rated “5 nm”




(b) Filters rated “10 nm”

Figure 7. Removal efficiency measured by gold nanoparticle challenge test for commercially available filters built around polyethylene media. (a) Filters with “5 nm” retention rating labels challenged with 5 nm gold nanoparticles, (b) Filters with “10 nm” retention rating labels challenged with 10 nm gold nanoparticles.

## 4. CONCLUSION

A novel method of rating the retention of lithography process filters below 30 nm was established. The method utilizes gold nanoparticles, which are detected using ICP-MS (for influent and effluent concentrations) and dynamic light scattering (to verify particle size). Electron microscope images confirm both the test particle size distribution and the absence of nanoparticle aggregation during retention challenge testing. Retention ratings that proceed from new and conventional test methods are in agreement for commercially available Pall filters that were rated at 30, 20, and 10 nm. Moreover, consistency in microbridge defect removal results suggest that filter retention ratings established via the new method can be confidently used by the lithography process engineer as a guide for selecting appropriate filtration products.

Large disparities in the removal efficiencies and retention rating labels of other commercially available filters indicate an urgent need to establish a standard method for rating filters that will be used in both present and future lithography process technology nodes. The gold nanoparticle challenge test is a promising method that utilizes established and well-understood techniques and elements that offer a high degree of confidence and repeatability in analysis.

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