How believable are reported concentrations of 1 ppt?

by Robert P. Donovan

One ppt stands for a "part per trillion," or one part in 10^{12}. It's the type of magnitude that you eventually get used to after repeatedly hearing or reading it, even while not fully comprehending its impact—like the numbers associated with the national debt, the gross national product or the federal budget.

One frequently hears ppt, or even sub-ppt, used in specifying the sensitivity of contemporary sensors or analyzers such as a gas chromatograph/mass spectrometer (GC/MS) or an inductively coupled plasma/mass spectrometer (ICP/MS) for measuring the concentration of impurities in cleanroom environments or process fluids.

So just how impressive are such detection limits? Consider 1 ppt expressed in terms of some common, everyday metrics. One second of time represents 1 ppt of about 32 millennia (320 centuries or 32,000 years) [3600 s/hr x 24 hr/day x 365.25 days/yr x 1000 yrs/millennium @ 3.2×10^{10} s/millennium; 10^{12} s π 3.2×10^{10} s/millennium = 32 millennia].

Finding a needle in a haystack sounds like a simpler problem than zeroing in on a specific inch between Earth and Venus, or isolating the unique properties of each distinctive second in 32 millennia.

But is it? How difficult is it to measure a ppt? It depends a lot on the sample volume and the concentration of the units to be counted. For example, the atomic density of silicon is about 5×10^{22} silicon atoms/cm^3. An impurity concentration of 1 ppt therefore implies the presence of about 5×10^{10} impurity atoms/cm^3, a fairly large-sounding number of atoms occupying a rather small space.

To make an accurate concentration measurement requires not just detecting impurity atoms having a distinctive identifying signature, but also not counting the non-impurity atoms making up the sample—yet knowing their concentration.

Intuitively, the seemingly large number of impurity atoms in just a modestly sized volume of silicon would appear capable of generating a detectable signal, assuming that the matrix silicon atoms surrounding the impurity do not interfere with the detection of the impurity.

The number of air molecules under standard conditions is about 2.5×10^{19}/cm^3 [air density = 1.2×10^{-3} g/cm^3; the molecular weight of air = 29]. The number of silicon atoms in a 0.1 µm diameter sphere of silicon is about 2.5×10^{7}. Thus, detecting one 0.1 x µm diameter silicon particle in 1 cm^3 of air corresponds to a number concentration sensitivity of 1 ppt.

Today's commercially available condensation particle counters (CPC) easily make this measurement. A CPC operating at a flow rate of 0.1 cfm samples 47 cm^3 of air/s so that a 0.1 cfm CPC that reports a particle concentration of forty-seven 0.1µm diameter particles per cm^3 is detecting 1 ppt of silicon atoms in air.

Let's simulate the haystack properties by those of fibrous filter media. The length of fiber in a unit volume of porous fibrous media is given by [ref 1]:

$L = 4\alpha/ \pi d_f^2$
where:
L = length of fiber in 1 cm^3 of filter media (cm/cm^3)
α = fiber volume/total volume = the packing density (-)
d_f = fiber diameter (cm).

For a haystack composed of 1 mm thick stalks of hay and a packing density of 0.1 (a rather dense haystack), L is 12.7 cm/cm^3. A 5-cm long needle buried in a one-cm^3 haystack represents a fractional length of just 0.4 (5/12.7) or 4 parts per 10. To be a ppt magnitude search problem, this haystack, assuming the same packing density, would have to consist of stalks having a total length of about 5×10^{12} cm, corresponding to a volume of 4×10^{11} cm^3 (5×10^{12}/ 12.7)—a stack having a base of about 75 m x 75 m and a height of about 75, a truly gigantic pile of hay.

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References

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