Development of New Calibration Scales for CH_3Br and CH_3Cl

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Atmospheric and oceanic mixing ratios of methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) have been measured by CMDL since 1994. Efforts to develop calibration scales for these molecules began in 1993. Two gravimetrically prepared standards served as the basis for the calibration scales from 1994 to 2001. During that time, it was discovered that CH_3Br and CH_3Cl mixing ratios can change with time in Aculife-treated aluminum cylinders, particularly at parts per trillion (ppt) levels. Efforts to enhance the scales by preparing new standards in both Aculife-treated aluminum and stainless steel cylinders have recently been made. Two different types of stainless steel cylinders and aluminum cylinders that showed relatively slow rates of CH_3Br change were used. Three new primary standards (prepared directly from reagent-grade starting material) were prepared (Figure 1). Five secondary standards (prepared from primary or secondary standards, not from pure reagent) were prepared at ppt levels. These new standards were used to confirm that mixing ratios of CH_3Br in some of the original standards had changed with time. They also showed that one of the CH_3Br primaries did not drift and agrees well with the new primaries. The resulting CH_3Br scale has reduced scale differences between CMDL and Scripps Institution of Oceanography. It is anticipated that stable, robust scales can be maintained by periodically preparing new secondary standards in stainless steel cylinders from various primaries and by continuing to monitor the relative differences between primaries.

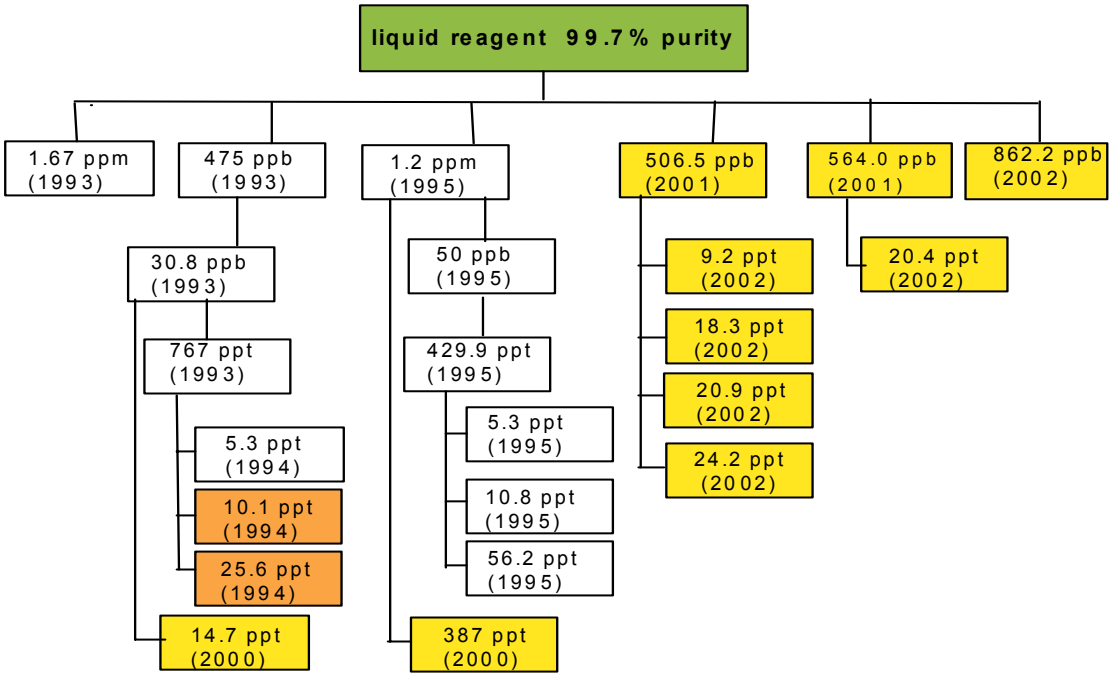

Figure 1. Family tree of gravimetrically prepared CH_3Br and CH_3Cl standards showing recent standards (yellow) and those primarily used to define the previous scale (orange).