

Stable Formaldehyde Calibration Mixture & Associated Analytical Challenges



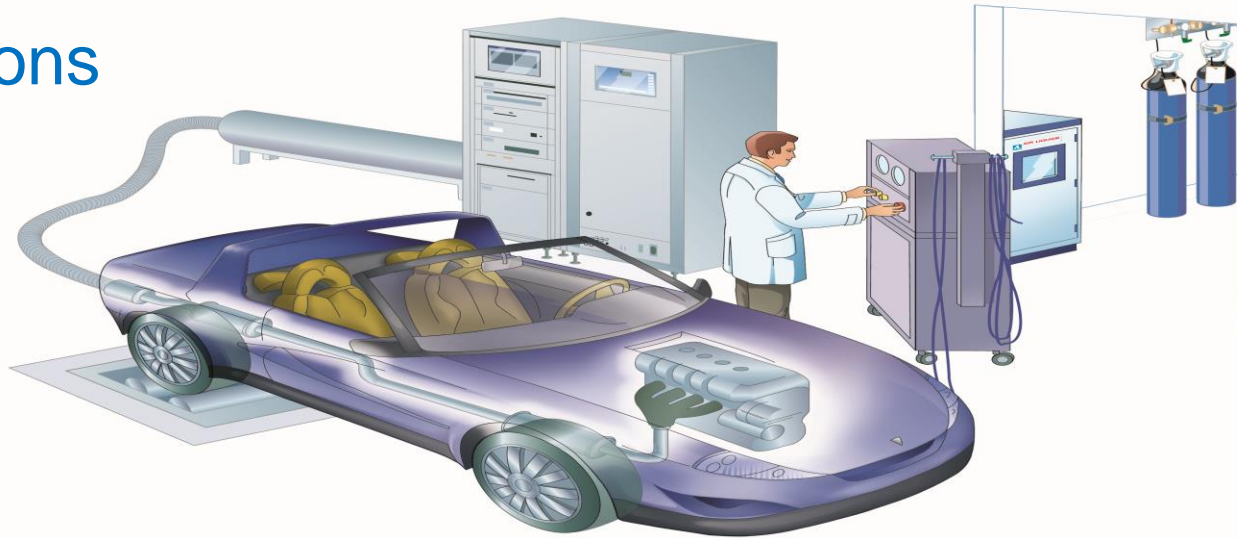
Anuj Kumar & Ken Wong

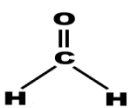
Delaware Research & Technology Center

May 31st 2016

Overview

- Why Formaldehyde?
- Challenges
- Stabilizing Formaldehyde in a Gas cylinder
- Conclusions





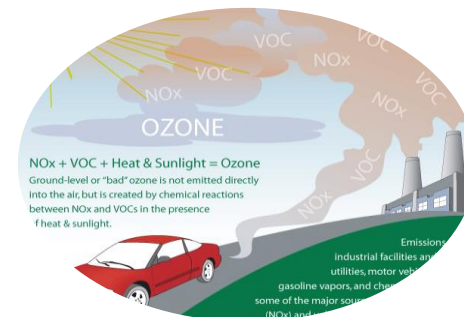
Why Formaldehyde ?



Mainly from
Human Activities



Highly toxic &
Potentially Carcinogenic



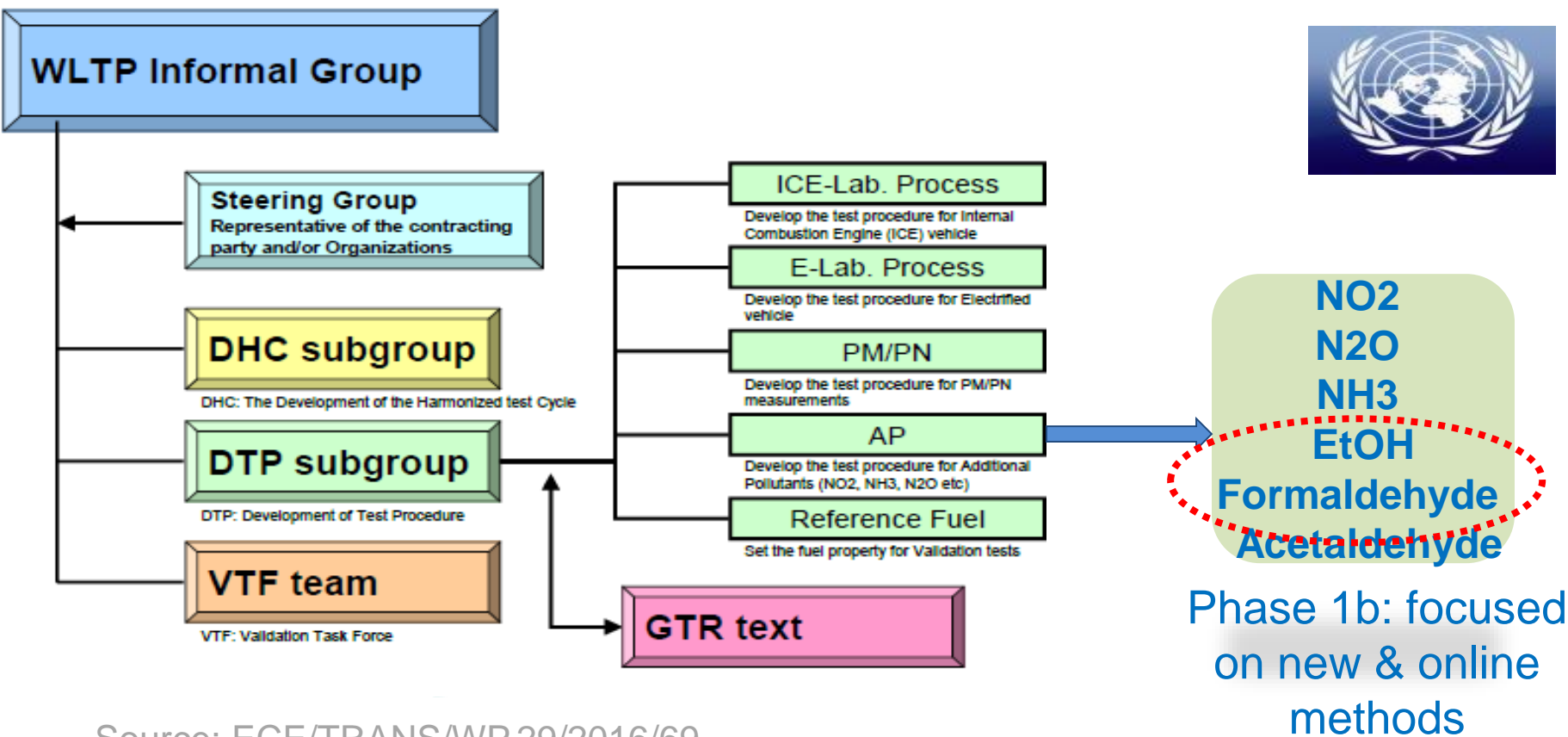
Ozone
Precursor

Increased vehicle emissions of aldehydes is attributed to ethanol mix fuel.

EU gasoline standard (EN228) allows 10% ethanol blend by volume

Ethanol is one of the major renewable fuels for transportation

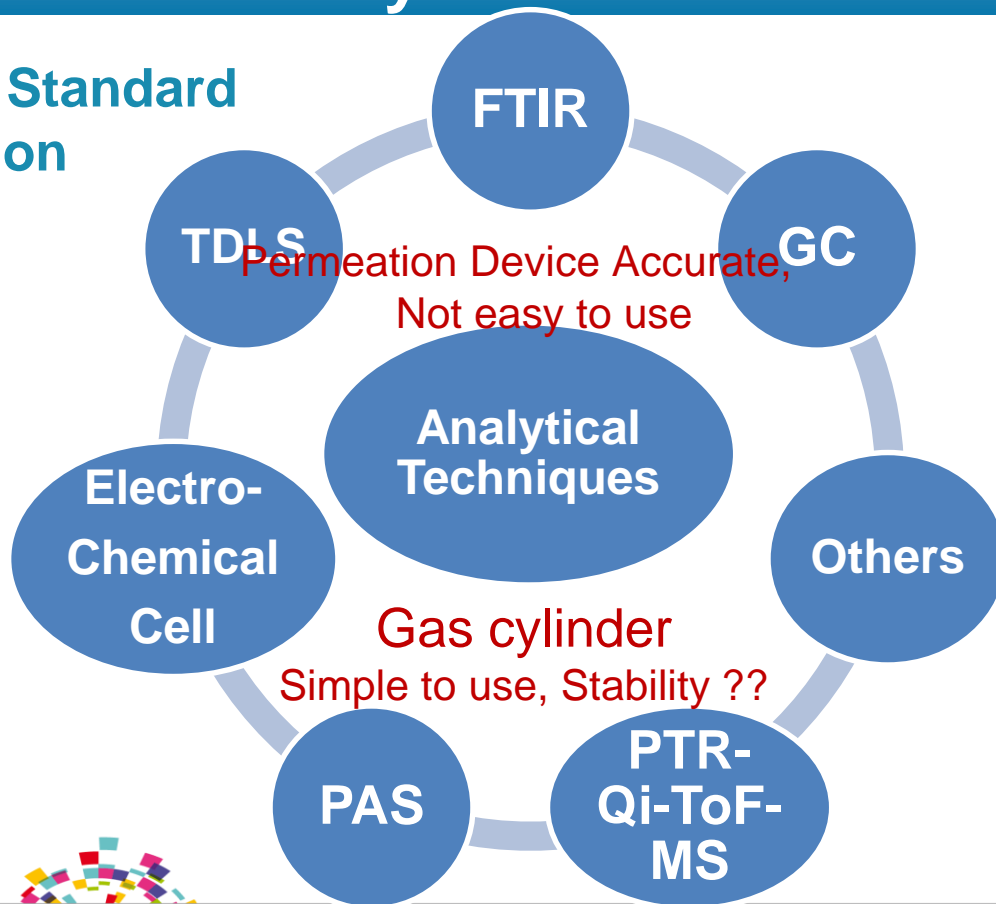
WLTP: Additional Pollutants (AP)



Source: ECE/TRANS/WP.29/2016/69

Formaldehyde: Instrumental Methods

... NEED a Gas Standard
for Calibration



Stability of Calibration Mixtures

Change in Concentration < Analytical Uncertainty

■ Cylinder conditions

- cylinder pressure
- cleanliness of cylinder
- reactivity of the inner surface

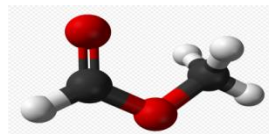
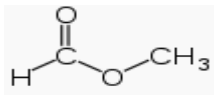
■ Mixture components

- reactivity between themselves
- reactivity with the cylinder
- concentration
- chemical nature

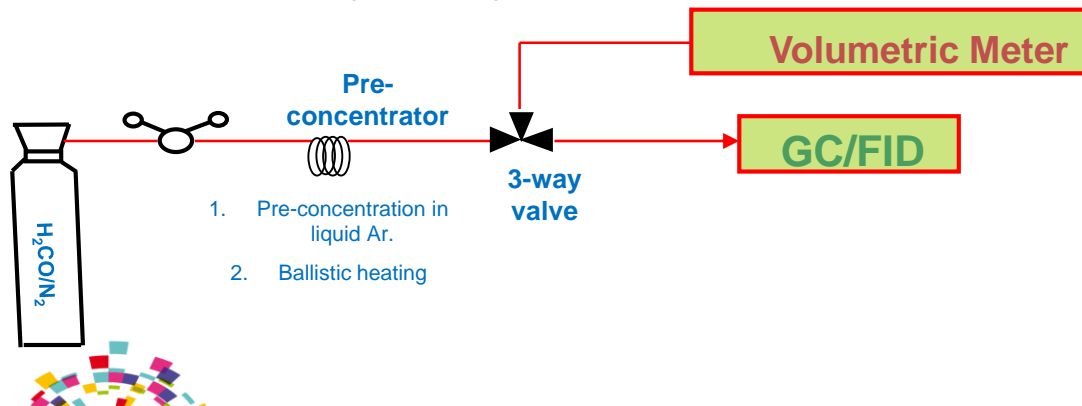


~Formaldehyde Instability

- Significant amounts of methyl formate was observed in **IMPROPERLY prepared Al cylinders.**

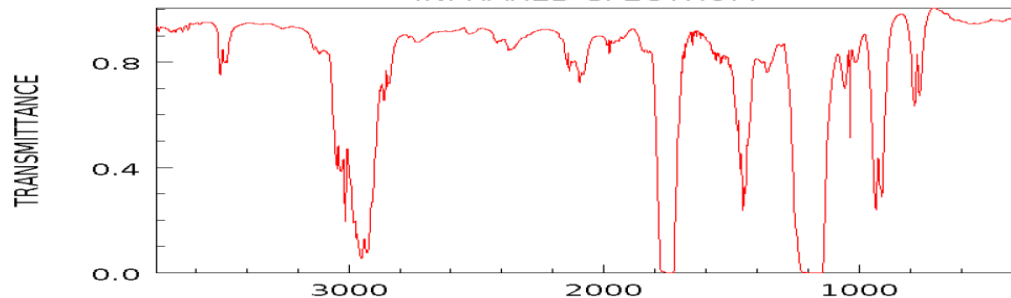


- Methyl formate interferes with formaldehyde FTIR analysis
- Methyl formate was analyzed by GC/FID

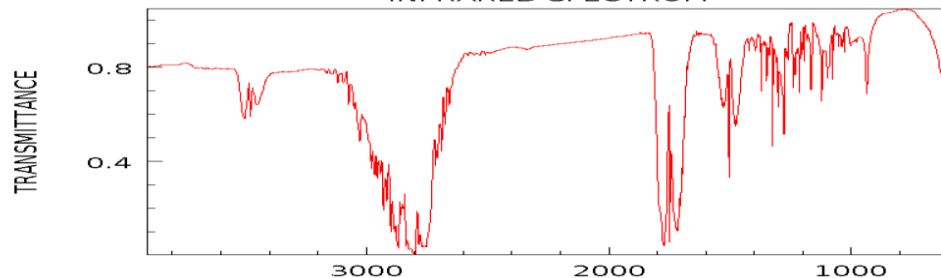


Methyl Formate & Formaldehyde IR Spectra

FORMIC ACID, METHYL ESTER
INFRARED SPECTRUM

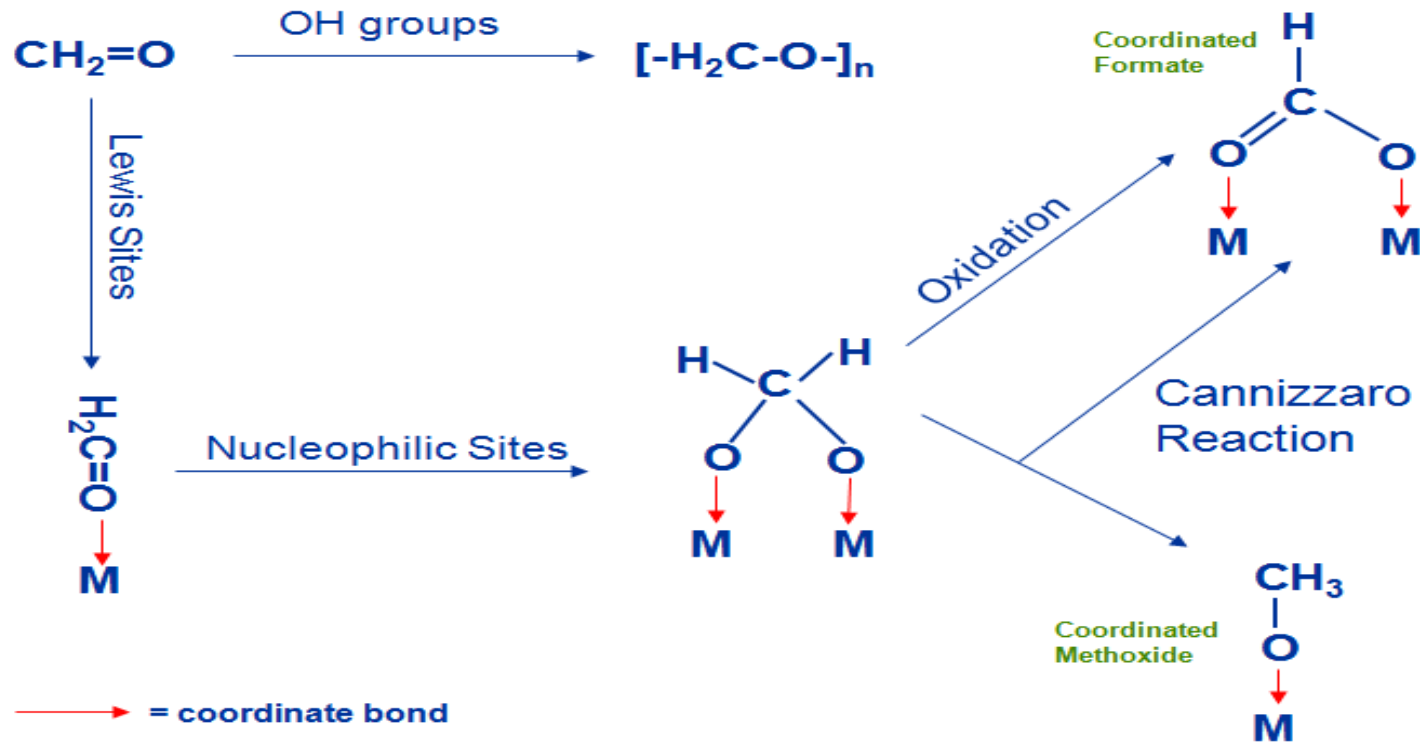


FORMALDEHYDE
INFRARED SPECTRUM



Air Liquide's formaldehyde cylinders are low in
methyl formate (< 1ppm)

Formaldehyde on Oxide Surface



Adapted from: Busca, G, *et.al.*, *J. Am. Chem. Soc.*, **109**, p 5197 (1987)

Stabilizing Formaldehyde in Gas Cylinders

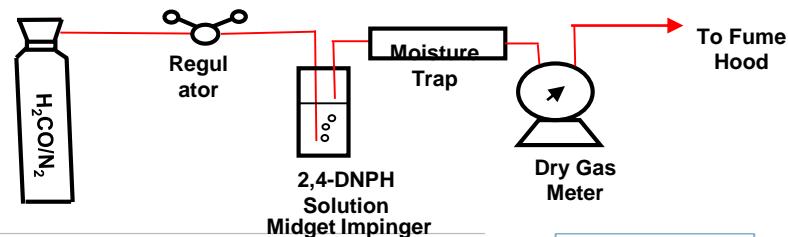
- Air Liquide Technology: **Aculife VIII** for formaldehyde
 - Specially prepared Aluminum cylinder
 - No secondary passivation was necessary
 - All formaldehyde cylinders were blended using a proprietary blending process.
 - Nitrogen was used as the balance gas.
 - Well established **EPA TO-11** method applied for analysis



DNPH Impinger Gas Sampling

■ EPA Method TO-11

- Trapping solution: 0.4% (w/v) of 2,4-DNPH in acetonitrile/4M HCl
- Bubble the gas into the trapping solution at the rate of ~ 1L/min
- Collect the sample for 10 – 30 minutes
- Derivatization of carbonyl compounds by 2,4-DNPH
- 2,4-DNPH was purified by recrystallizations in acetonitrile
- The DNPH derivative is analyzed for aldehydes by HPLC.
- At least 3 collections for each cylinder.



HPLC Calibration & Analysis

Linear, >0.9999
correlation coefficient

Residual $<1\%$
for each standard

Instrument drift $< 1\%$
between injections

10 ppb
detection limit

RSD $< 1\%$
 ≥ 3 injections/standard

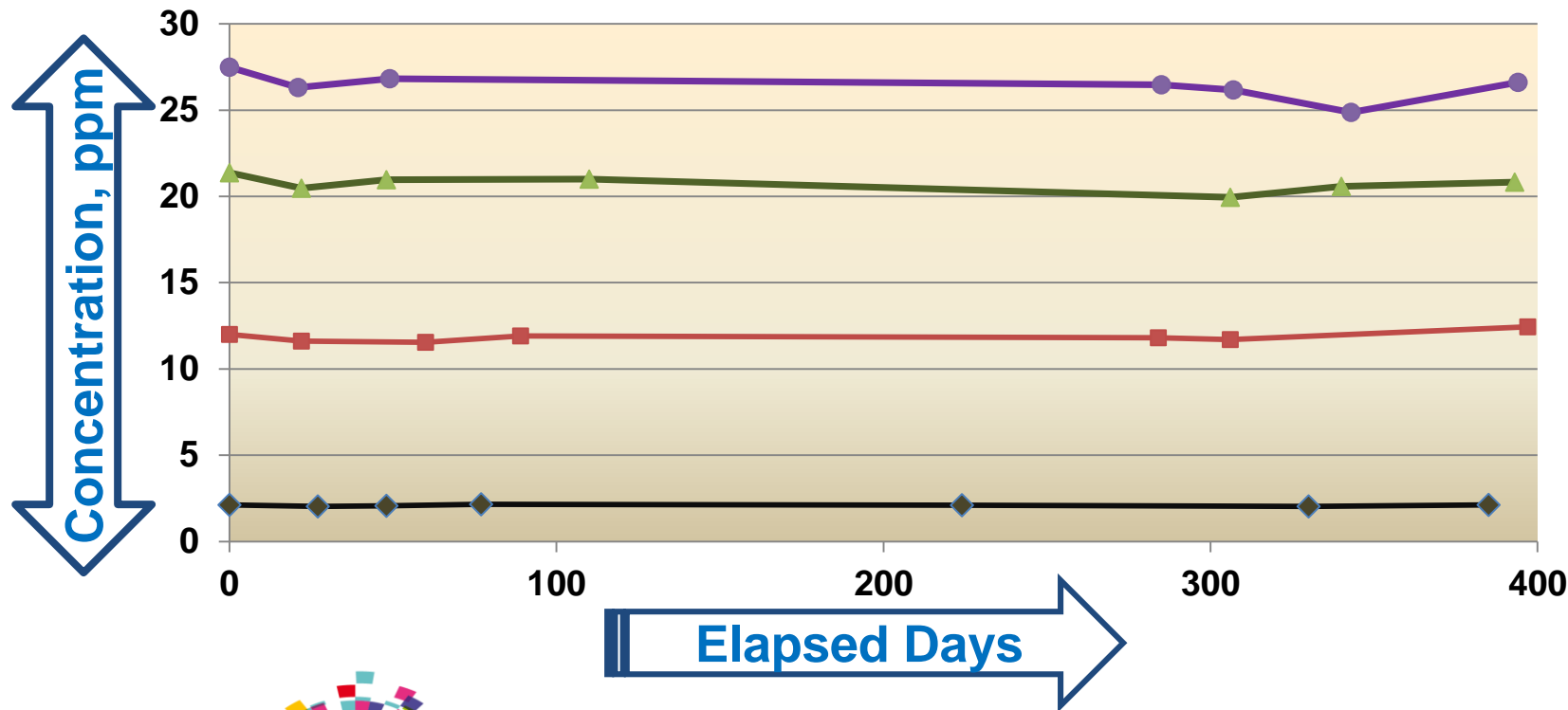


| Expected concentration | # 1 | # 2 | # 3 | Average | RSD |
|------------------------|------|------|------|---------|------|
| 30 ppm | 33.4 | 33.2 | 33.0 | 33.2 | 0.6% |
| 3 ppm | 3.06 | 3.07 | 3.07 | 3.07 | 0.2% |

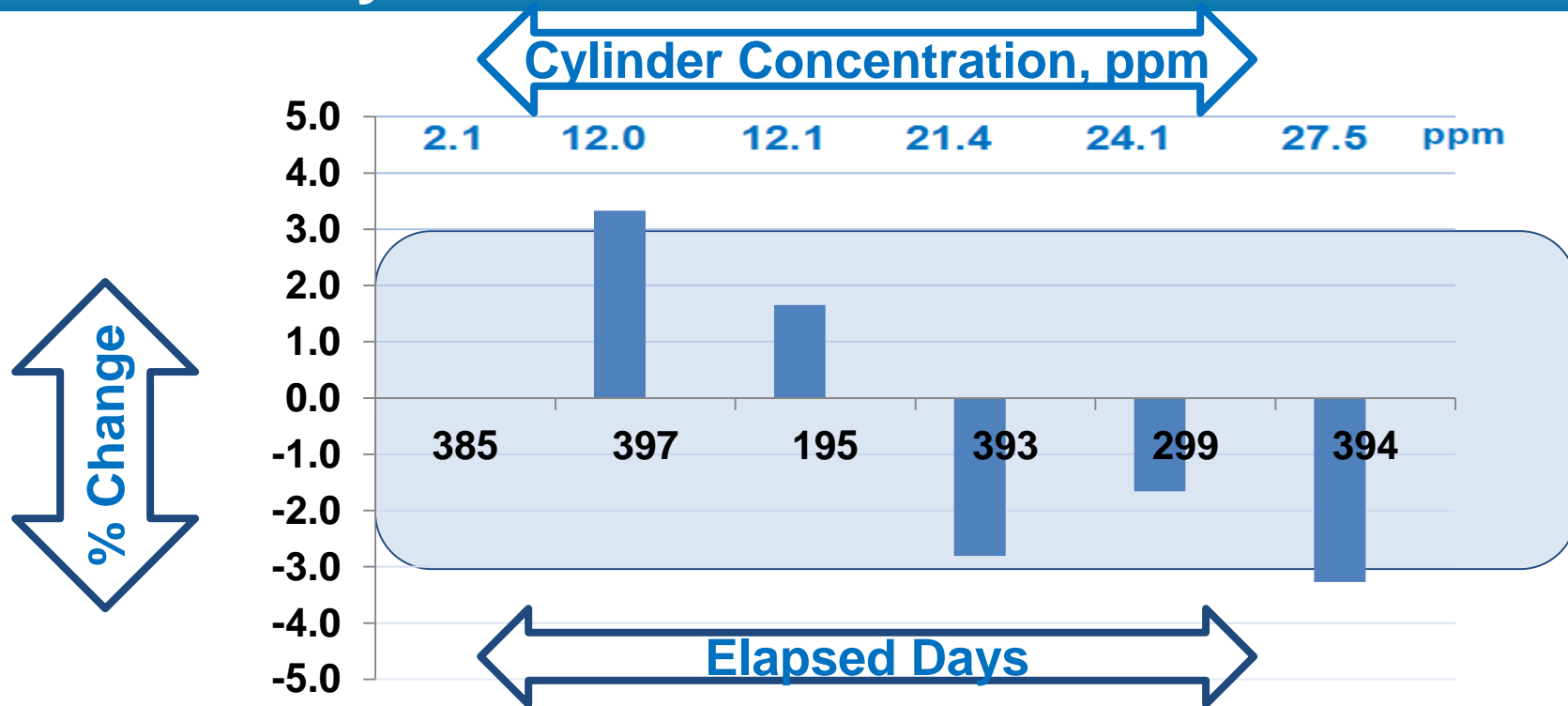


Formaldehyde Stability in Gas Cylinder

2-30 ppm formaldehyde stability shown over 1 year



Formaldehyde Deviation Over 1 Year



Change in formaldehyde over a period of 1 year is about 3%.

BIPM Study

GAS2013



ISO/TC 158
Analysis of gases

NEN

Progress towards an international comparison of formaldehyde in nitrogen standards: stability studies and purity analysis of potential transfer standards

In addition to being an important indoor air pollutant, formaldehyde is a ubiquitous component of both the remote atmosphere and polluted urban atmospheres. With new regulations coming into force, as well as an increased monitoring network, the demand in gaseous formaldehyde standards at low concentration (from 1 nmol/mol to 10 μ mol/mol) is increasing. Dynamic standards as well as static gas mixtures in this range are currently being developed at a number of National Metrology Institutes (NMIs), which plan to demonstrate their comparability through a CCQM Key Comparison, coordinated by the BIPM.

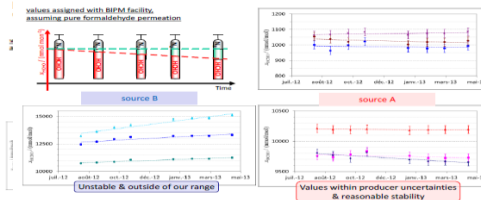
BIPM facility

The BIPM facility is based on continuous weighing of formaldehyde permeating from a paraformaldehyde tube maintained at constant temperature in a pure nitrogen flow. It was setup early 2010 and has been validated in a series of measurements over one year.



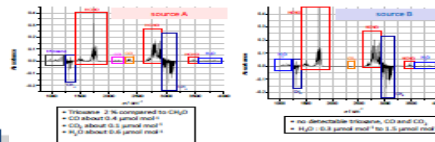
Cylinders Stability Study

Stability tests over 10 months together with purity analysis have been performed on a group of certified gas cylinders containing formaldehyde in nitrogen at 1 and 10 μ mol/mol, coming from two production sites. Results show promising stability for one sub-set of cylinders.



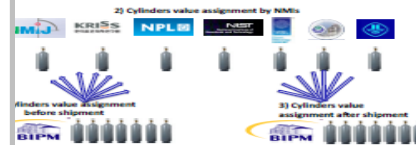
FTIR purity analysis

Fourier Transformed InfraRed spectroscopy has been used to perform a quantitative analysis of the impurities. In the dynamic mixtures, it demonstrated the need for an accurate quantification of trace water. In some cylinders, traces of trioxane were identified. Our HCHO analyser based on CRDS was tested to demonstrate the absence of interference with trioxane.



International comparison CCQM-K90

BIPM will coordinate the international Key comparison QM-K90, planned to start in 2014. Transfer standards of HCHO (roten at low μ mol/mol) nominal values will be value assigned the BIPM and by participants to define their degree of agreement.



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More information on this and related projects can be obtained at www.bipm.org

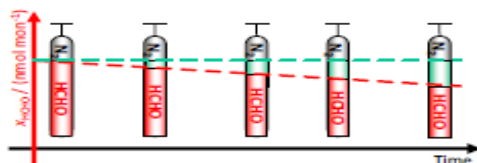
Source: BIPM



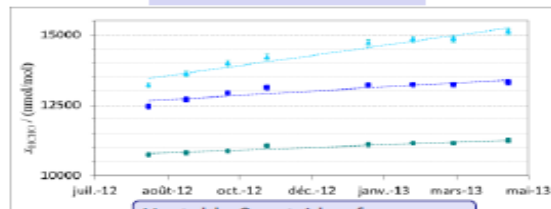
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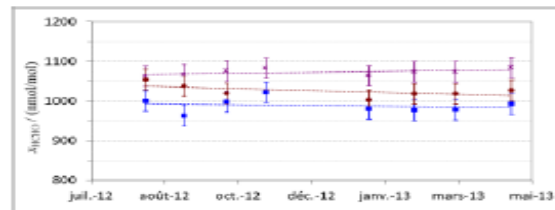
values assigned with BIPM facility,
assuming pure formaldehyde permeation



source B



Unstable & outside of our range



source A



Values within producer uncertainties
& reasonable stability

Source: BIPM



Conclusions

- Stable formaldehyde in Aluminum gas cylinder
- Tested successfully in the range of 2 to 30 ppm
- Well established **EPA TO-11** method applied for analysis
- The shelf lives of these mixtures are at least one year.
- Stable formaldehyde mixtures are low in methyl formate.
- BIPM evaluated the Air Liquide cylinders





Stand # 1534

Automotive Testing Expo

Research & Development

Opening new ways

THANK YOU FOR YOUR ATTENTION!

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