

HF instrument calibration

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DLS
LAB

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Introduction

Presence of HF molecule in atmosphere of nuclear facility is signature of UF_6 enrichment activity. Backpack instrument was developed to measure concentration of HF during IAEA inspections. In present paper we'll consider the instrument developed calibration.

Traditionally measurements of molecular concentration in TDLS are calibrated using calibrated gas mixtures. For dipole molecules such as HF, NH_3 , H_2O , etc. this procedure is more complicated.

Such molecules have long-range dipole-dipole interaction. It results in complex formation and molecular absorption on surfaces. Hence, gas mixture under consideration is hetero-system. In case of HF it contains HF molecules, HF complexes, HF- H_2O complexes, HF absorbed by instrument surfaces, HF diluted in water absorbed on these surfaces. In this case HF molecules concentration depends on many parameters: temperature, total HF concentration (HF plus HF complexes), humidity, environment, etc. Mentioned above complicates very much calibration procedure.

Goal of present poster is to consider procedure of concentration measurements in TDLS and to demonstrate that TDLS is primary standard to measure impurity concentration.

Bouguer law

Bouguer law: a relationship describing the rate of decrease of flux density – $W(x)$ of a plane-parallel beam of monochromatic radiation as it penetrates a medium which absorbs at that wavelength

[\[http://roland.lerc.nasa.gov/~dglover/dictionary/b.html\]](http://roland.lerc.nasa.gov/~dglover/dictionary/b.html)

$$\frac{\partial W_\nu(x)}{\partial x} = -\sigma(\nu) N_{HF}(x) W_\nu(x) \quad \sigma - \text{absorption cross-section, } N - \text{molecules number density}$$

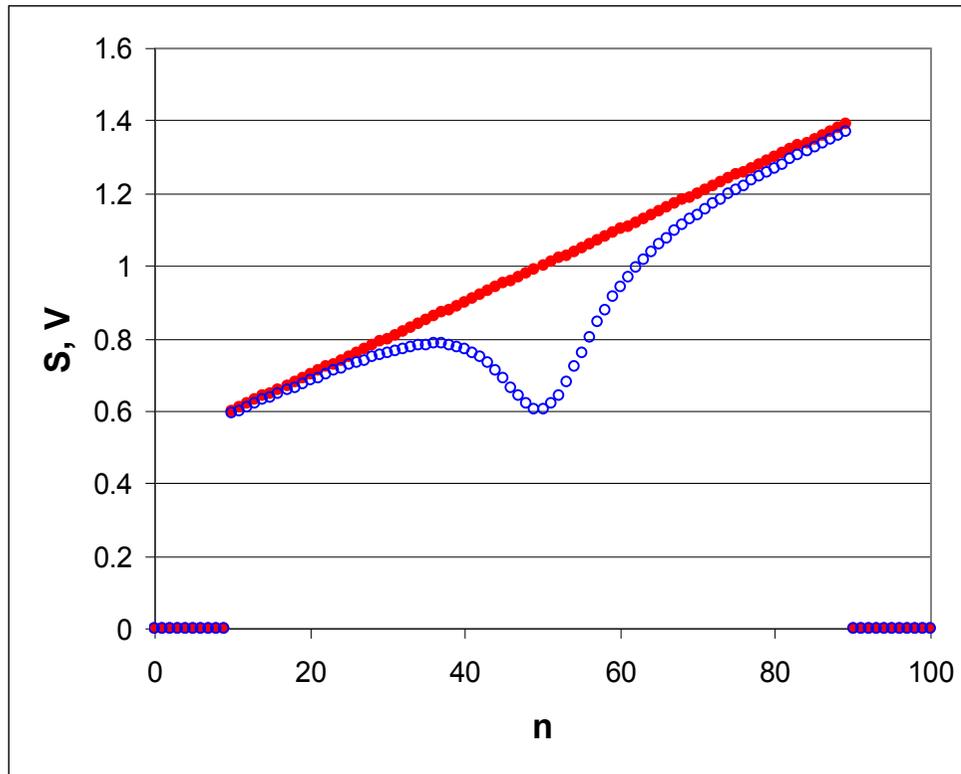
For homogeneous number density distribution ($N = \text{const}$)

$$W_\nu(L) = W_\nu(0) \exp[-\sigma(\nu) N_{HF} L]$$

This is law, it is true always for monochromatic radiation. DL radiation is not monochromatic. It contains broad spontaneous emission component. We've checked this situation and demonstrated that Bouguer law is valid for TDLS up to 10^{-3} level.

Absorbance

Bouguer law: $W_L(\nu) = W_0(\nu) \exp[-\sigma(\nu)N_{HF}L]$



Red line – W_0 , blue open cycles – W_L .

Now we can introduce absorbance α directly proportional to molecules density number N_{HF}

$$\alpha(\nu) = -\ln \left[\frac{W_L(\nu)}{W_0(\nu)} \right] = \sigma(\nu)NL$$

It is direct measurement. Hence, it is valid.

Absorption cross-section

At atmosphere pressure P_0 HF line in use has Lorentz shape determined by 3 spectroscopic constants

$$\sigma(\nu) = \frac{S\gamma_{air}P_0}{\pi\left[(\nu - \nu_0)^2 + (\gamma_{air}P_0)^2\right]}$$

HITRAN spectral database [HITRAN (v11.0), <http://cfa-www.harvard.edu/hitran>]
 HF molecule 2-0 R(0) spectral line spectroscopic constants

Parameter	Meaning	Value
ν_0	Vacuum wavenumber	7788.856 cm ⁻¹
S	Intensity	4.79 10 ⁻²⁰ cm ⁻¹ /(mol cm ⁻²)
γ_{air}	Air-broadened half-width (HWHM)	0.09 cm ⁻¹ /Bar
I_{err}	Uncertainty	0.001 < $\Delta\nu$ < 0.01 cm ⁻¹ 5 % < ΔS < 10% 10% < γ_{air} < 20%

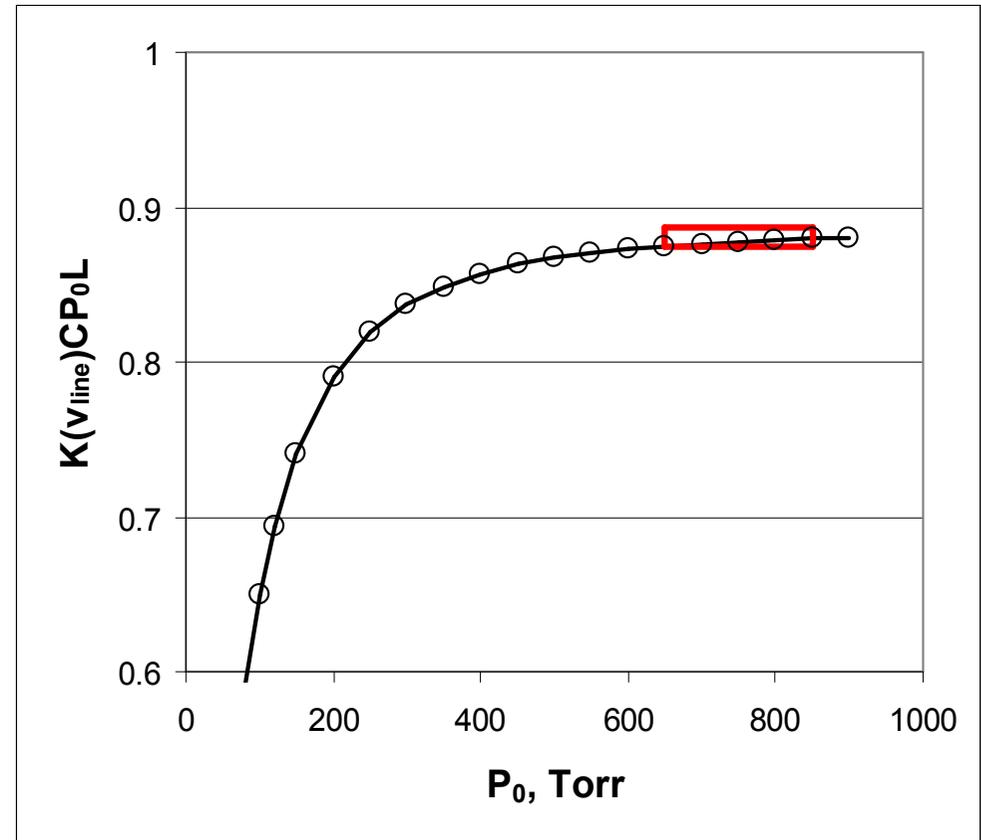
All parameters were measured by several groups, passed intercomparison procedure and can be considered as cosmological constants known with presented accuracy.

Atmosphere pressure influence

Pressure dependence of absorbance in spectral line center – $K(\nu_{line})CP_0L$ of gas mixture under investigation ($C = 500$ ppm) for normal atmosphere ($T = 23^\circ\text{C}$, absence of HF, 50% humidity). For model Lorentz profile the absorbance is constant and can be calculated.

$$K(\nu_{line})CP_0L = \frac{S}{\pi\gamma_{air}} \frac{P_{HF}}{P_0} L =$$
$$= \frac{S}{\pi\gamma_{air}} C_{HF} L = 0.887$$

Real line shape (Voigt profile) differs from model one and absorbance pressure dependence can be observed.



Red rectangular represents error of absorbance variations due to possible changing of atmosphere pressure. For HF concentration measurements it leads to error of less than 2 % relative.

Temperature influence

Temperature influences HF measurement due to two mechanisms: temperature dependences of molecule ground state population (temperature dependence of S) and broadening coefficient (temperature dependence of γ_{air}). For linear HF molecule and R(0) line following relations are valid.

$$S(T) = S(T_{ref}) \frac{T_{ref}}{T}$$

$$\gamma_{air}(T) = \gamma_{air}(T_{ref}) \left(\frac{T_{ref}}{T} \right)^n$$

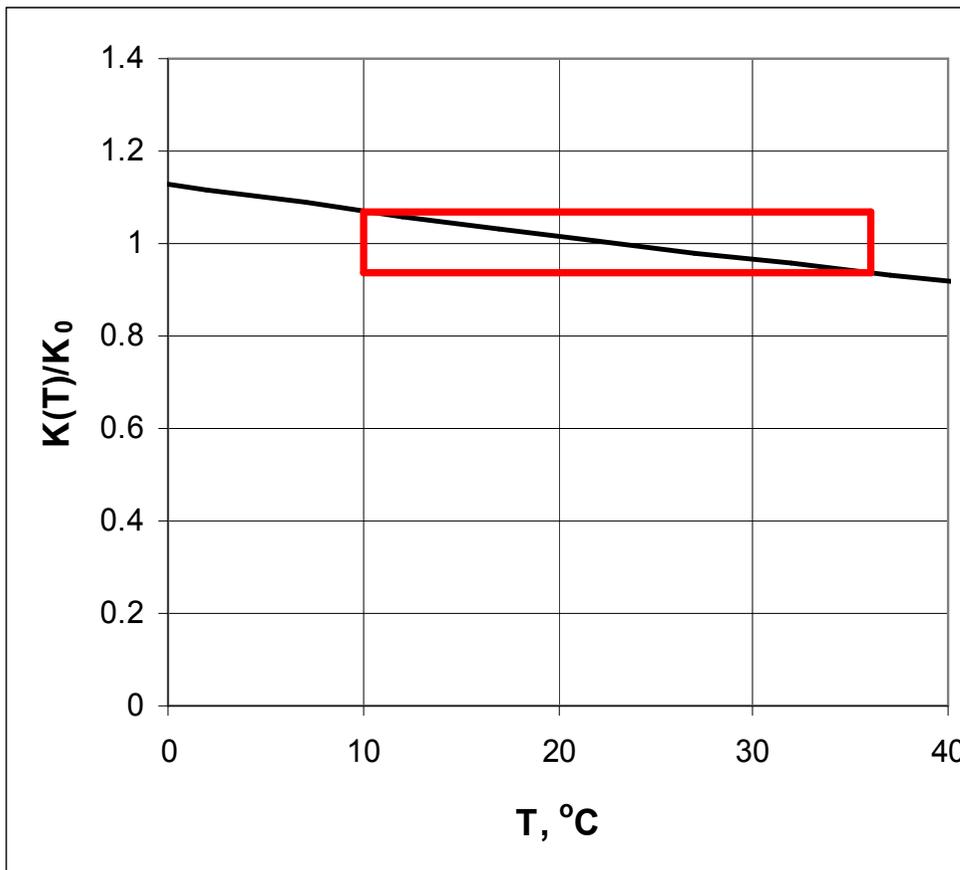


Figure (black curve) presents humidity influence on HF measurement.

Red rectangular represents error of HF concentration measurements due to possible temperature changing. It is less than 7 % relative.

Humidity influence

As it was mentioned above, water absorption has no influence on HF concentration measurement for particular HF spectral line in use. However, humidity influences on HF absorption because of HF line broadening due to collisions between HF and H₂O molecules.

$$\frac{K(P_{H_2O})}{K_0} = \frac{[\gamma_{air}(1 - C_0) + \gamma_{H_2O}C_0]}{[\gamma_{air}(1 - C_{H_2O}) + \gamma_{H_2O}C_{H_2O}]}$$

Here $C_0 = 1.4\%$ is water vapor concentration in normal atmosphere (23°C, 50% humidity) HF line broadening coefficient γ_{H_2O} is unknown. However, γ_{self} can be used as estimate due to dipole-dipole interaction in both cases.

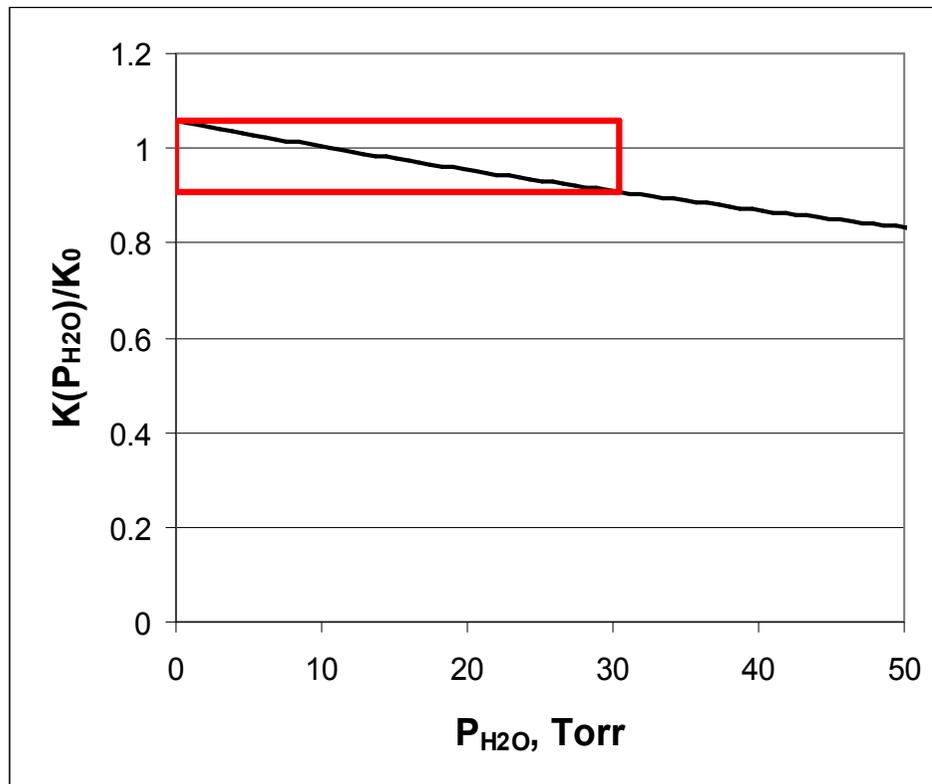


Figure (black curve) presents humidity influence on HF measurement.

Red rectangular represents error of HF concentration measurements due to possible changing of humidity. It is less than 10 % relative.

Physical laws in TDLS

Bouguer law: $W_\nu(L) = W_\nu(0) \exp[-\sigma(\nu)N_{HF}L]$ For TDLS valid up to 10^{-3}

Absorbance measurement $\alpha(\nu) = -\ln\left[\frac{W_\nu(L)}{W_\nu(0)}\right] = \sigma(\nu)N_{HF}L$ Is valid by measurement procedure.

Cross-section shape is known and all its parameters can be considered as cosmological constants.

$$\sigma(\nu) = \frac{S\gamma_{air}P_0}{\pi[(\nu - \nu_0)^2 + (\gamma_{air}P_0)^2]}$$

When transmission spectrum is measured, HF molecule concentration can be obtained straightforward.

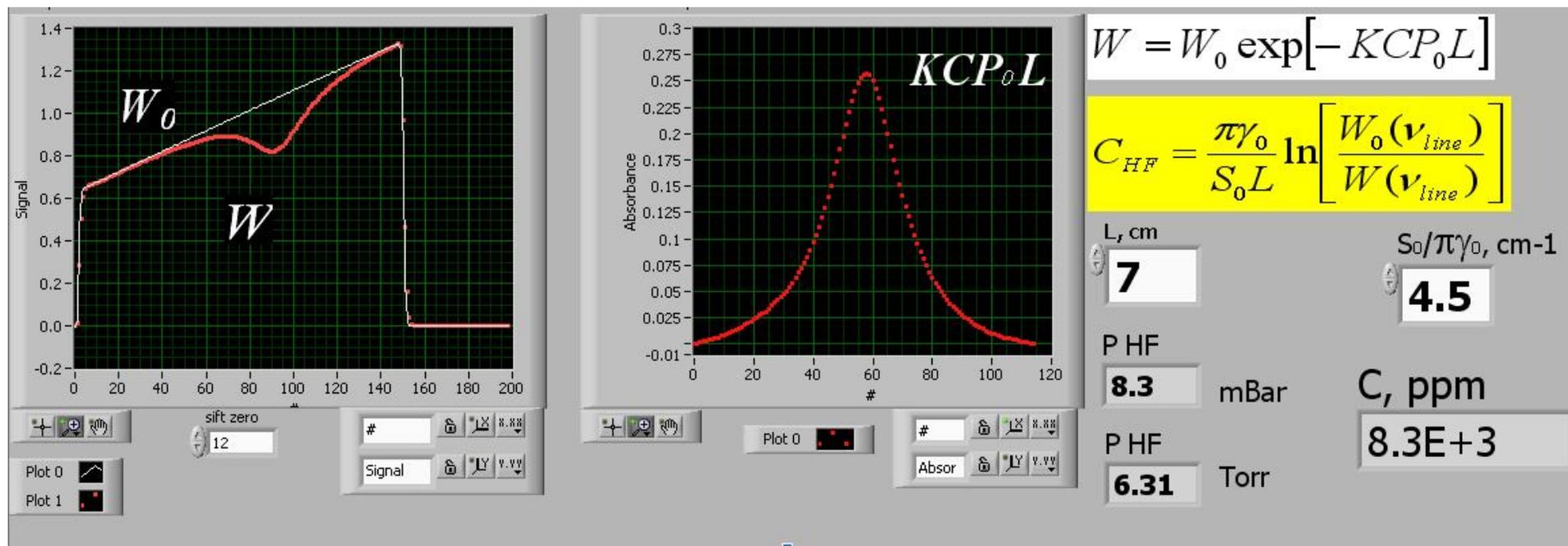
$$C_{HF} = \frac{0.22cm}{L} \ln\left[\frac{W_0(\nu_0)}{W(\nu_0)}\right]$$

Conclusion: Using procedure described TDLS instrument do direct measure of HF concentration. It is based on physical laws and cosmological constants. Hence it can be considered as primary standard with accuracy 20 %.

Reference channel calibration

Signal waveform in reference channel. HF absorption line can be observed.

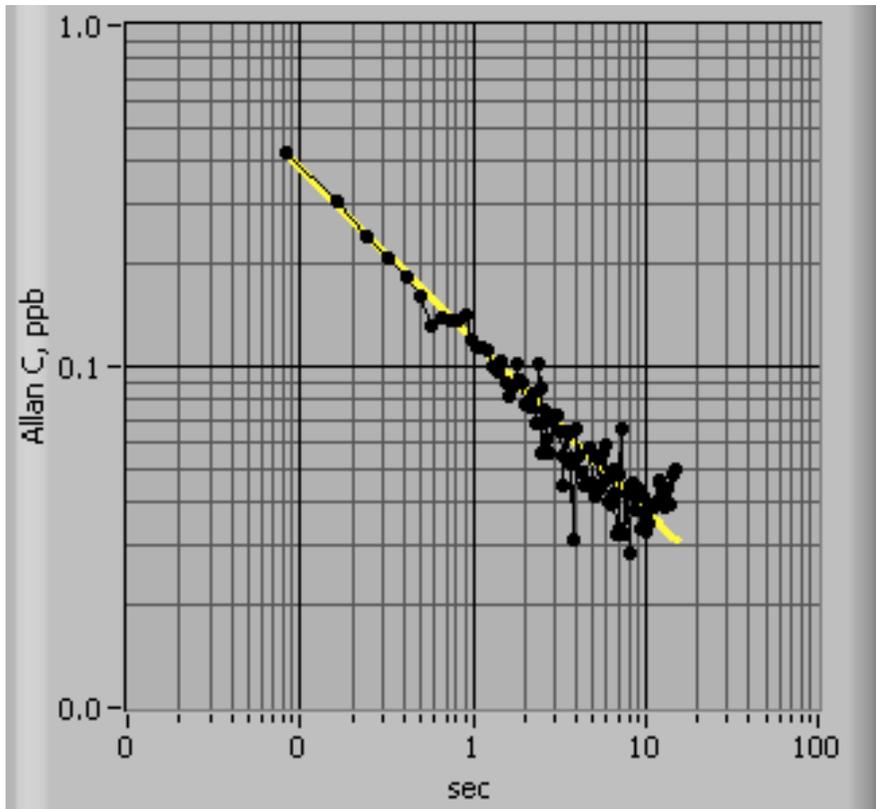
HF absorption line shape in reference channel: $L = 7$ cm, $P_0 = 1$ Bar.



When transmission spectrum is measured, HF molecule concentration and its partial pressure can be obtained straightforward: in present case 0.83 % and 8.3 mBar, respectively. HF pressure in reference cell is not constant subject to its temperature variation. **During instrument operation reference channel is calibrating continuously.**

Minimum detectable concentration

In presence of recorded signal noise - ΔS , NEC (Noise Equivalent Concentration) can be introduced by definition:



$$NEC = \frac{0.22cm}{L} \ln \left[\frac{S + \Delta S}{S} \right] = \frac{0.22cm}{L} \frac{\Delta S}{S}$$

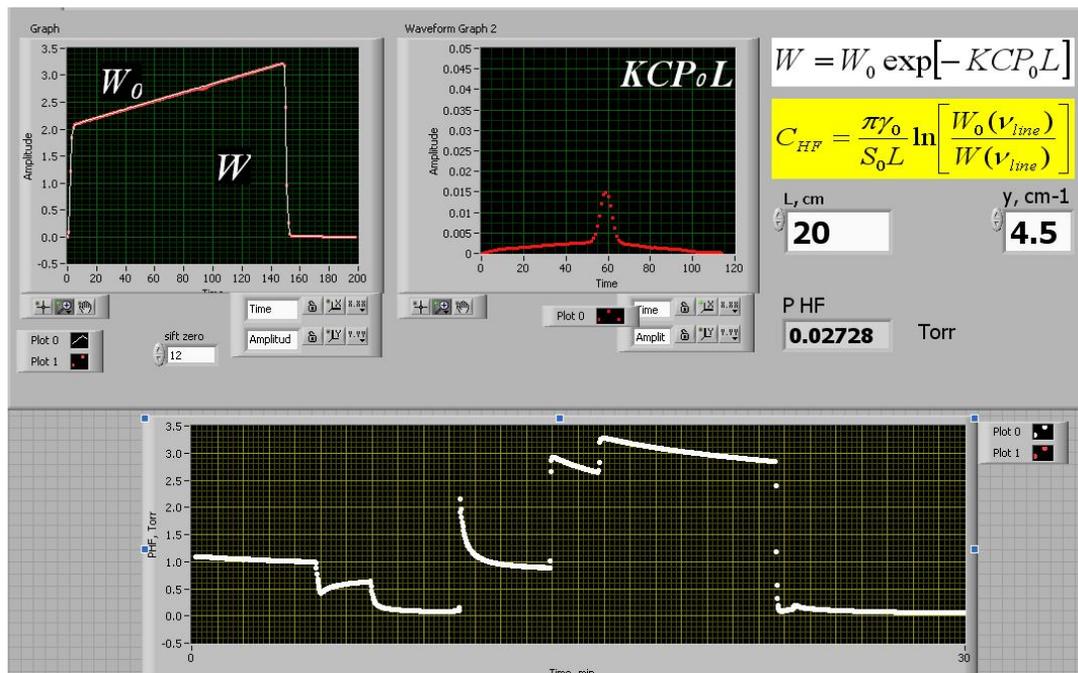
NEC determines minimum detectable concentration.

Left - NEC as function of averaging time.

Results were obtained in Albuquerque with instrument under consideration.

For averaging times above 0.07 sec NEC below 0.5 ppb was achieved. It is reverse proportional to square root of averaging time. For averaging time 10 sec, NEC is equal to 0.04 ppb.

Calibration test at Kurchatov institute



Pure HF in stain-steel cell with sapphire windows.

HF pressure as measured by TDLS. Simultaneously pressure was measured by monometer. Within monometer accuracy its results were in agreement with TDLS.

$t = 10.5$ min cell was filled with 2.2 Torr of HF. Quick HF concentration decrease after filling is due to HF absorbing on cell walls. Then HF was added 2 more times with slower HF decrease. Left side of picture shows results of previous experiment. The cell was filled with HF. $t = 4.8$ min the cell was connected to pump showing HF concentration decrease. $T = 5$ min pumping was stopped and increase in HF concentration was observed due to HF desorbing from cell walls.

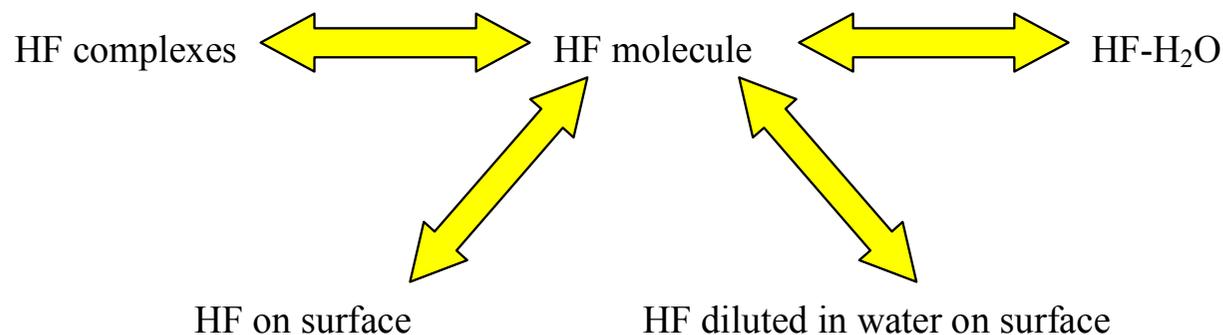
Some estimations: molecules number in cell at 1 Torr is $5 \cdot 10^{18}$. HF molecules number on cell walls for 1 molecular layer is $2 \cdot 10^{18}$. Hence, one molecular layer corresponds to 0.4 Torr. Presented results demonstrate that **several molecular layers were absorbed on the cell walls. Number of layers depends on HF pressure inside cell.**

HF in gas mixture samples

TDLs detect only HF molecules. In real HF gas mixture samples HF is presenting in different forms

In atmosphere with presence of HF one has to consider: HF molecules and HF polymers (mainly HF dimers).

Due to atmosphere humidity HF-H₂O complexes will be presented.

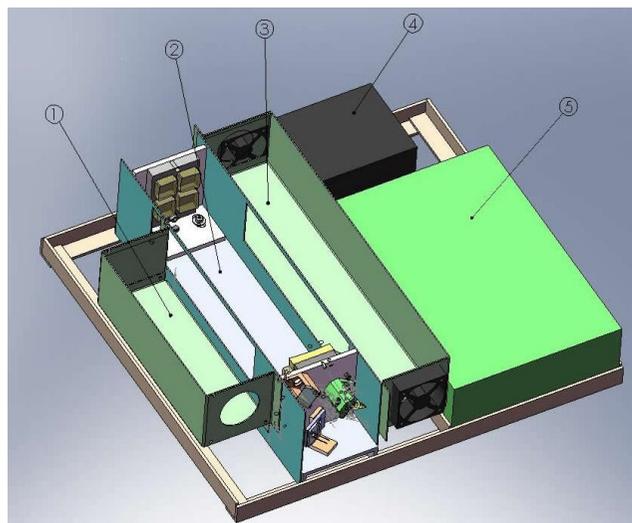
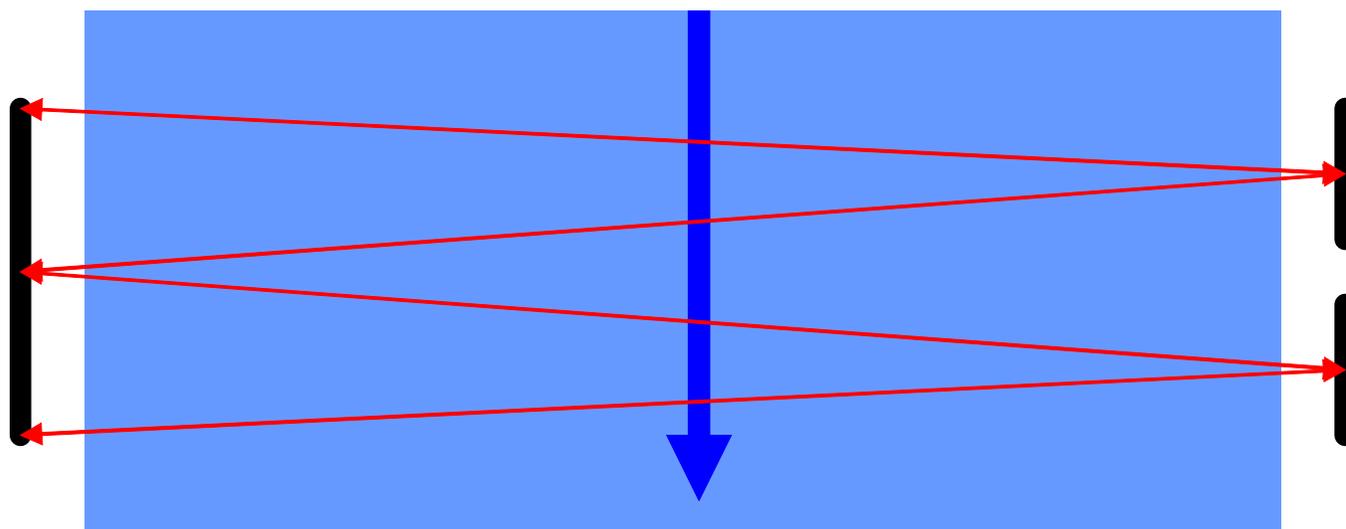


Presence of any surface will result in HF absorbing on it and HF dilution in water adsorbed on this surface.

As result, HF molecules concentration in samples is function of many parameters (temperature, humidity, environment, etc.).

Worse: HF will chemically react with dielectric mirrors (last layer on mirror is SiO₂) reducing their reflectivity.

Possible solution

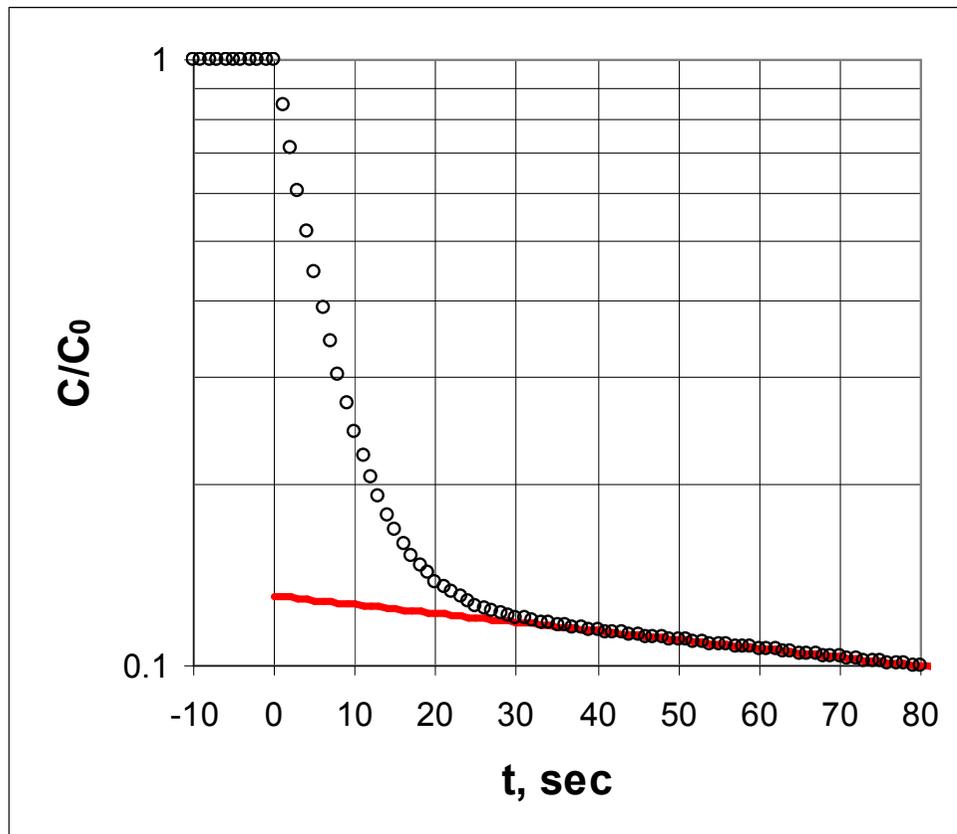


Gas flow (blue) is directed perpendicular to optical axes of cell to reduce time of gas exchange. Gas flow rate was 60 l/sec. Hence, HF interaction with cell components is reduced as much as possible.

Gas flow has to be laminar to prevent HF molecules to achieve mirrors and other cell components and dust particles to achieve mirrors. Laminar gas flow was visually controlled by cigarette smoke injected in the cell.

Filling factor calibration

To prevent these interactions special gas flow was organized to prevent HF interaction with mirrors and cell walls as well as interaction of dust and moisture with mirrors for field applications. As result not all cell volume was filled by gas flow. So, filling factor F has to be calibrated. Filling factor is determined by gas flow geometry and doesn't depend on particular molecule. For filling factor calibration we've used methane impurity (it is simpler than HF).



The cell was filled with methane gas mixture. Constant value of measured concentration can be observed. At $t = 0$ ventilator was switched on and outer air (low methane) removed mixture with high methane concentration. Methane concentration as measured by TDLS dropped quickly during some sec. Long concentration tail is due to methane diffusion. Interpolating this tail to $t = 0$ (red line) fill factor was determined. It was found 0.8 – 0.9.

Conclusion

All steps of data recording and processing in TDLS instrument to measure HF concentration in atmosphere were analyzed. Pressure, temperature, and humidity dependence of measured values were considered. Based on physical laws, known cosmological constants, analysis, and calibrations performed, it was shown that TDLS is primary standard of HF concentration in atmosphere measurement with accuracy 20%. Noise equivalent HF concentration was 0.04 ppb for 10 sec averaging time using TDLS instrument developed. Tests at facilities demonstrated possibility to detect undeclared activity using instrument developed.