BIPM Capacity Building & Knowledge

Transfer Program 2019 BIPM - TÜBİTAK

UME Project Placement

REPORT

Project Name	2019 BIPM - TÜBİTAK UME Project Placement
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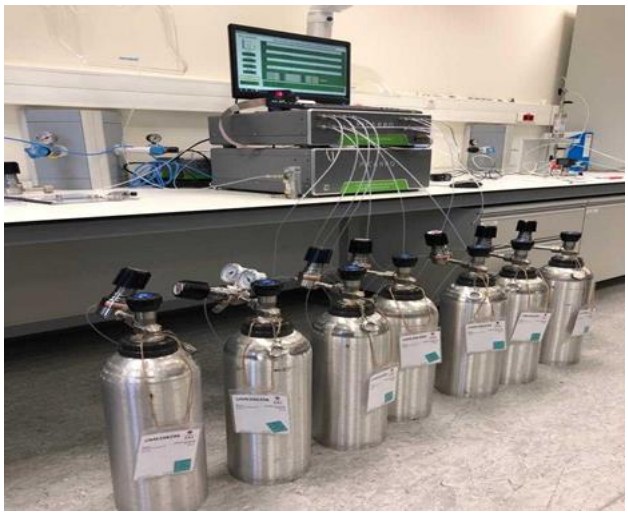
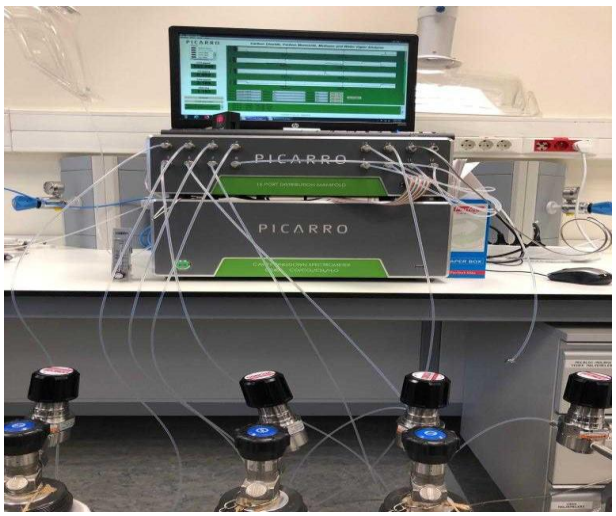
Motivation & Introduction

This project aims to develop the technical skills and capabilities of the National Calibration and Measurement Center (SASO-NMCC) researchers / technicians in the gas measurements by developing in-house knowledge transfer program. This initiative contains NMIs such as TÜBİTAK UME best practices to be transferred to SASO-NMCC team through technical workshops as well as hands-on training. Worth mentioning that SASO-NMCC participates in inert compressions to build the right capabilities to publish its CMCs.

Research

Training program was completed at TUBITAK UME covering three main practices on measurements of greenhouse gases using CRDS. The program consists of theoretical, practical and uncertainty calculation trainings.





Introduction about CRDS

The Picarro G2401 greenhouse gas concentration analyzer enables simultaneous measurements of CO2, CH4, CO with part-per-billion (ppb) sensitivity and negligible drift over months of operation. Cavity ring down spectroscopy (CRDS) is a sensitive technique that makes use of an optical cavity to measure absorptions on the order of parts per million and beyond. By choosing appropriate tunable light sources, we can measure the spectroscopy and kinetics of the chemical systems. It was originally developed as a tool for determining the high reflectivity of mirrors and has since been widely employed in measuring weak spectroscopic transitions and concentrations of trace gases.

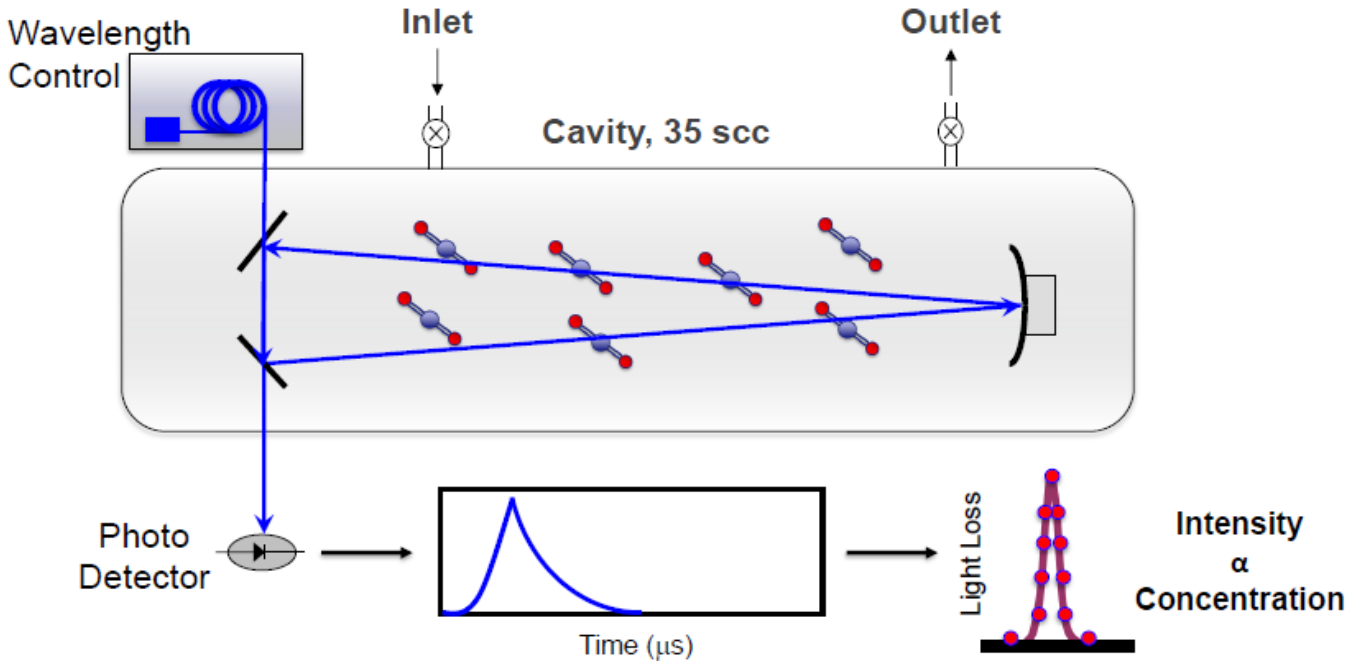
Advantages of CRDS

*High sensitivity due to the multipass nature (i.e. long path length) of the detection cell.
*Immunity to shot variations in laser intensity due to the measurement of a rate constant.

*High throughput, individual ring down events occur on the millisecond time scale.
*Compact, less expensive and more portable.

The principle of working

1) A Continuous wave (CW) laser emits a directed beam of light energy through an ultra-high reflective mirror into the absorption cell (cavity).
2) The light reflects back and forth between two ultra-high reflective mirrors multiple times, up to a total path length of 100 kilometers.
3) Once the photodiode detector “sees” a preset level of light energy, the light source is diverted from the cavity.
4) On each successive pass, a small amount of light or ring-down signal emits through the second mirror and is feel by the light detector.
5) Once the light "rings down", the detector achieves a point of zero light energy in milliseconds and the measurement is complete.



Performance of the CRDS Picarro G2401

Guaranteed Performance Specifications in dry air	**CO_2**	**CO**	**CH_4**	**H_2O**
Precision (5 sec / 5 min / 60 min, 1σ) Reference gas not needed	< 50 ppb / 20 ppb / 10 ppb	< 15 ppb / 1.5 ppb / 1 ppb	< 1 ppb / 0.5 ppb / 0.3 ppb	< 30 ppm / 5 ppm / n/a
Max Drift at STP (over 24 hrs. / 1 month) (peak-to-peak, 50-minute average) Reference gas not needed	100 ppb / 500 ppb	10 ppb / 50 ppb	1 ppb / 3 ppb	100 ppm ± 5% of reading
Max Uncertainty using Reference Gas (1 hr average, 2σ) WMO Data Quality Objective for GAW Stations	< 50 ppb	< 2 ppb	< 1 ppb	n/a
Reproducibility (10 min, 1σ) [1] ICOS Atmospheric Station Specification	< 50 ppb	< 1 ppb	< 0.5 ppb	n/a
Automated Determination of Dry Mol Fraction	Included	Included	Included	n/a
Operating Range	0 – 1000 ppm	0 – 5 ppm	0 – 20 ppm	0 - 7 %v H_2O
Guaranteed Specifications Range	300 – 500 ppm	0 – 1 ppm	1 – 3 ppm	0 - 3 %v H_2O
Measurement Interval	< 5 seconds	< 5 seconds	< 5 seconds	< 5 seconds
Rise/Fall time (10 - 90 % / 90 - 10%)	< 5 seconds	< 5 seconds	< 5 seconds	< 5 seconds

It was accomplished during the training period:

1- Searching literature for CRDS device and identify the mechanism of operation of the device .

2- Discussion with experts on the device.

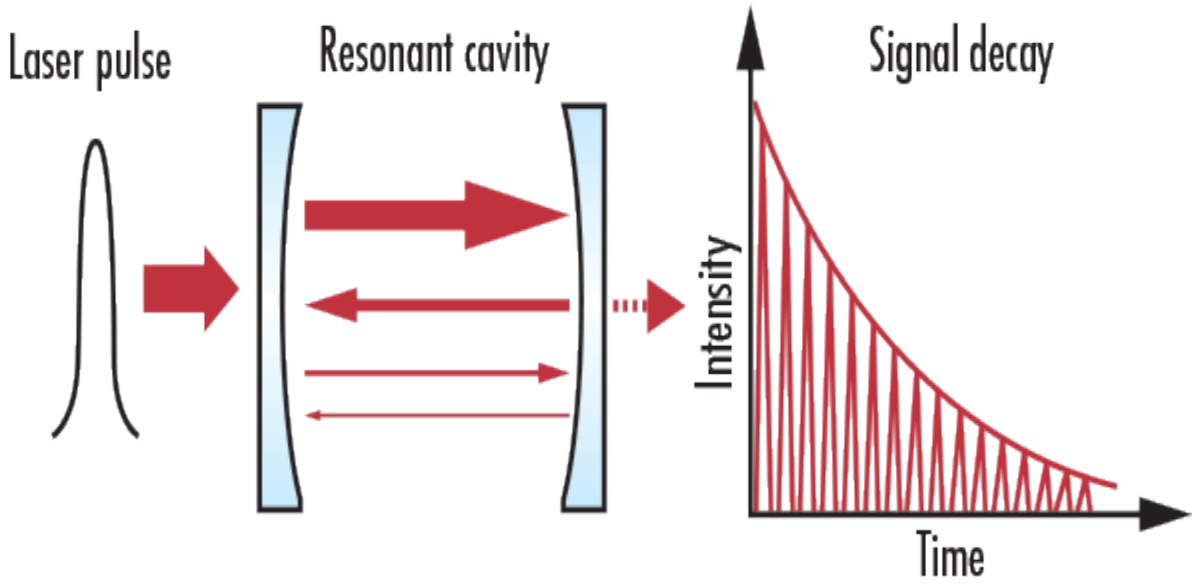
3- The basic parts of the device are identified as follows:

- Cavity with 3 high – reflectivity mirrors
- Laser Control
- Detector (photo detector)
- Auto sampler
- pump

4- The function of each part of the device has been identified as follows:

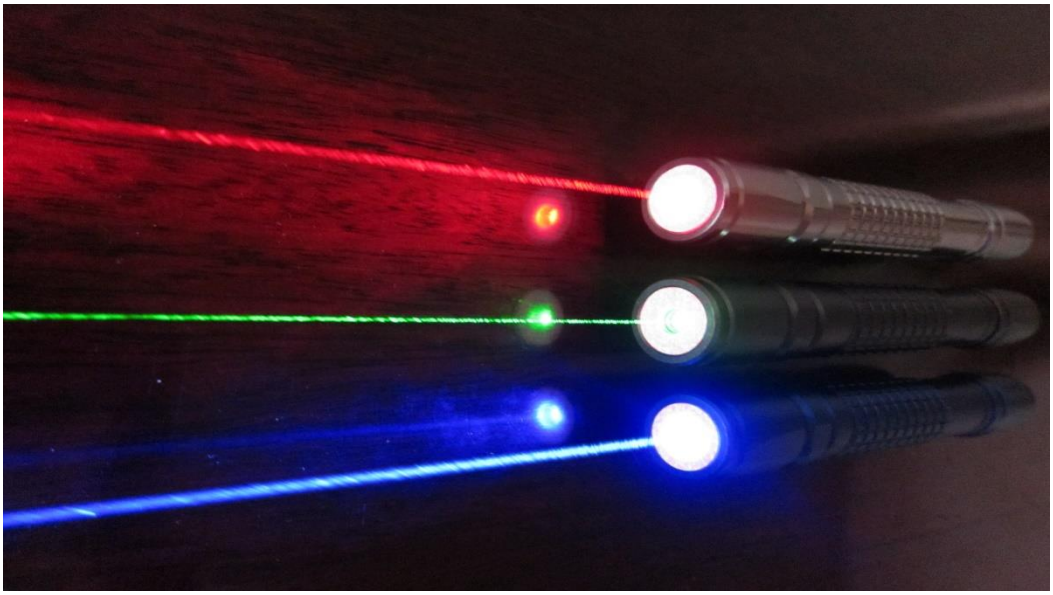
- **Cavity with 3 high – reflectivity mirrors** :

  Reflectivity Mirrors, are commonly used to improve beam profile and quality in non-stable resonators. The variable reflectivity of the mirror is a function of the radial distance from the center, with the highest reflectivity values found in the center. These variable reflectivity mirrors provide better modal discrimination and favor the oscillation of the fundamental mode over higher order modes.



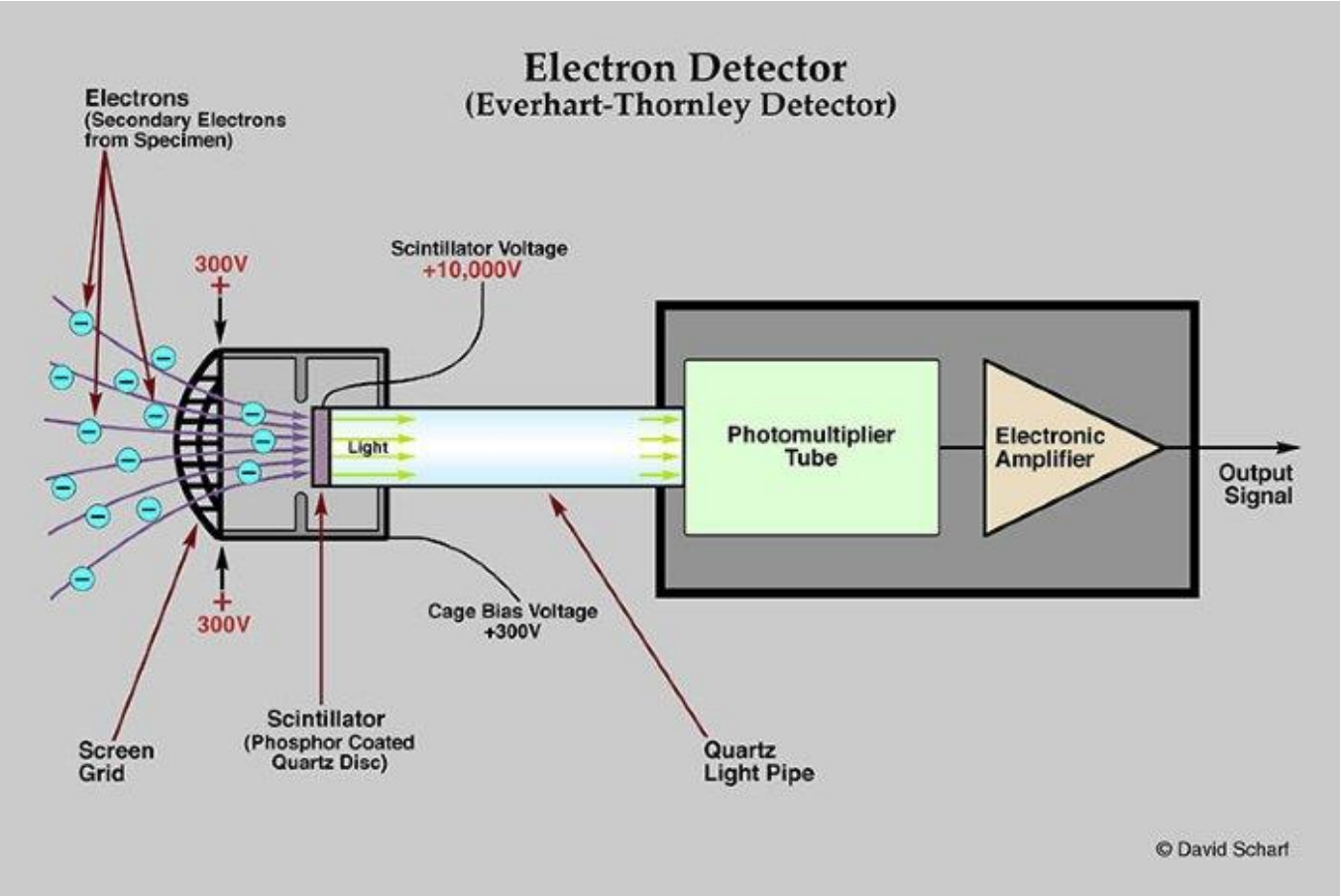
- **Laser Control**

A laser is device that emits light through a process of optical amplification based on the stimulated emission of electromagnetic radiation.



Detector (photo detector)

Photo detectors are used primarily as an optical receiver to convert light into electricity.



- **Auto sampler**
  A device that automatically loads collected samples (as for spectroscopic or chromatographic analysis) into a laboratory instrument.

- **Pump**
  A device which take the sample from atmosphere or cylinder to cavity.

Practical

CRDS was used for analysis (CO_2, CO, CH_4). All the uncertainty given below are standard uncertainty.

(Single point)

Reference cylinder code	Concentration ppm(CRM)	Uncertainty ppm(CRM)	Concentration ppm(dilution)	Uncertainty ppm
PSM499847 (CO_2)	1.00E+02	1.002E-01	1.0394E+01	2.2120E-02
UME298296 (CO)	9.911E+00	9.910E-03	9.911E+00	9.910E-03
PSM499834 (CH_4)	1.001E+03	1.001E+00	1.0394E+01	2.1262E-02

(Measurements result)

Unknown cylinder code	Concentration ppm	Uncertainty ppm
PSM499824 (CO2)	1.0137E+01	2.1609E-02
PSM499824 (CO)	9.7830E+00	9.8239E-03
PSM499824 (CH4)	1.0326E+01	2.1657E-02

* We did the analysis for single point according to standard (ISO 12963:2017) .

ISO12963 : Gas analysis – Comparison methods for the determination of the composition of gas mixtures based on one – and two – point calibration .

(multi point)

Reference cylinder code	Concentration ppm	Uncertainty ppm	Cylinder unknown	Concentration ppm	Uncertainty ppm
UME249367 (CO_2)	2.00E+02	2.00E-01	PSM499784	4.00E+02	4.00E-01
UME249431 (CO_2)	5.00E+02	5.00E-01			
UME249421 (CO_2)	7.00E+02	7.00E-01			

* We did the analysis for multi-point according to standard (ISO6143:2001)

ISO6143: Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures.

Introduction about method validation

Methods Validation: Establishing documented evidence that provides a high degree of assurance that a specific method, and the ancillary instruments included in the method, will consistently yield results that accurately reflect the quality characteristics of the product tested.

Method validation is an important requirement for any package of information submitted to international regulatory agencies in support of new product marketing or clinical trials applications. Analytical methods should be validated, including methods published in the relevant pharma capoeira or other recognized standard references. The suitability of all test methods used should always be verified under the actual conditions of use and should be well documented.

The method validation was applied on (CRDS) when we analyzed (CO).

The followings have been determined:

- LOD
- LOQ
- Recovery
- Precision
- Accuracy

Conclusions and Future Work

Proposed project aims to transfer the knowledge and skills gained in mentioned above program to SASO-NMCC team. In house knowledge transfer program is being developed to share best practice.

Acknowledgements

I would like to take this opportunity to express my thanks and appreciation to TUBITAK-UME and BIPM teams for their limitless support and for giving the opportunity to participate in such a beneficial program. Special thanks to my mentor Dr. Tanil Tarhan and to Dr. Erinc Engin, and thanks also to the team that working within the gas laboratory.