Use of HITRAN and UVACS databases for the task of precision ambient air control

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Abstract

Difference between concentration of gas substance calculated using HITRAN database in the infrared spectral region or using UVACS database in the ultraviolet spectral region from one side and concentration of measured standard reference material (gas in this case) from the other side can form several percents. At the same time e.g. accuracy of control of greenhouse gases should be not worse than parts of one percent. National metrological centers under the aegis of the BIPM organize the key comparisons for the purpose to increase the accuracy and to provide the traceability of measurements. Different metrological measures have to be undertaken to increase the accuracy of parameters of HITRAN or/and UVACS databases.

Introduction

Calibration of instruments based on spectral methods of analysis can be made with the help of two procedures: by means of standard reference materials (SRM) – calibration gas mixtures and by calculation with the use of absorption cross-sections or line parameters. Cylinders with gas mixtures and gas generators (dynamic or thermo-diffusion) are used most frequently for calibration. From the other side numerical data of absorption cross-sections or line parameters are used for numerical calibration. In several cases, only numerical calibration can be used for atmospheric open-paths analyzers as the most correct. Calibration of conventional or open-path multi-components gas analyzers with the use of gas mixtures is generally expensive because there is a need of big quantity of gas mixtures. That is why the use of spectral databases has a sense as for measurements of total content of substances in multi-components gas mixtures by means of open-path gas analyzers as well as for purposes of certification of gas mixtures in cylinders and also for calibration of conventional gas analyzers without use of SRM.

Databases and accuracy problems of available numerical data

Work to create database[1] of absorption cross-sections of atmospheric components (database UVACS) was preliminary completed in 1998.[1]

No	Molecule	Spectral Range, nm	No	Molecule	Spectral Range, nm	No	Molecule	Spectral Range, nm
1	H2O	120-189; 260-330нм	44	CCl4	174-275	87	CH3SSCH3	201-360
2	CO2	120-300	45	C2H5Cl	160-240	88	CH3SNO	190-430; 510; 545
3	O3	120,2-720,4	46	CH3CCl3	182-240	89	C2H5CHO	230-340
4	N2O	120-250	47	ClONO	235-400	90	(CHO)2	230,5-462,0
5	CO	120,0-206,5; 218,4-228,4	48	BrONO2	186-390	91	CH3COCHO	225-475
6	CH4	106-160	49	HONO	190-395	92	CH3COCH3	250-350
7	O2	140,8-250,0	50	ClNO2	190-370	93	CH3OOH	210-365
8	NO	186,3-226,8	51	ClNO	115-350	94	CH3ONO2	270-330
9	SO2	188,75-320,00	52	N2O5	200-285	95	C2H5ONO2	185-330

10	NO2	160-725	53	ClOO	242,5-470,2	96	n-C3H7ONO2	185-330
11	NH3	185-233	54	COCl2	116-160; 184,9-280,0	97	i-C3H7ONO2	185-330
12	PH3	194-236	55	COFCl	186-226	98	CH3O2NO2	200-325
13	HNO3	120-170,190-330	56	CH3Br	190-260	99	CH3CO3NO2	200-300
14	OH	282	57	CF2Br2	190-308	100	HCOF	220-295
15	HF	146-162	58	CF3Br	190-268	101	CF3COF	200-300
16	HCl	140-220	59	CHF2Br	210-255	102	Cl2O3	
17	HBr	170-221	60	HClO4	190-280	103	CH3CFCl2	190-228
18	HI	170-228	61	N2O4	185-390	104	CF3CHFCl	190-228
19	ClO	240-310	62	HO2NO2	190-330	105	CF3CHCl2	190-228
20	OCS	200-270	63	CS2	295-355	106	CF3CF2CHCl2	160-240
21	H2CO	225-376	64	HNCO	120-255	107	CF2ClCF2CHFCl	160-240
22	C2H6		65	ClO3	200-350	108	HCOCl	236,1-318,7
23	CH3D		66	NO3	400-691	109	CCl3CHO	200-360
24	C2H2	154-202	67	CCl3F	160-260	110	CF3COCl	200-330
25	C2H4		68	CCl2F2	174-226	111	CF2ClBr	190-288
26	GeH4		69	CClF3	160-220	112	CHBr3	190-310
27	HCN		70	CHCl2F	160-235	113	CF2BrCF2Br	190-280
28	C3H8		71	CHClF2	160-220	114	HOI	300-475
29	C2N2	110-170	72	CH2ClF	160-230	115	IO	415-470
30	C4H2		73	CCl2F-CClF2	160-250	116	INO	230-460
31	HC3N		74	CClF2-CClF2	160-235	117	I2	178-195
32	HOCl	215-375	75	CF3-CClF2	172-204	118	F2	210-370
33	N2		76	CF3-CH2Cl	160-245	119	ICN	210-300
34	CH3Cl	174-216	77	CH3-CClF2	160-245	120	HO2	184-260
35	H2O2	120-350	78	BrO	300,00-388,32	121	N3CN	120-200
36	H2S	160-270	79	BrCl	220-540	122	HN3	115-210
37	HCO OH		80	Br2	320-540	123	SCCl2	238-282; 387,25-560
38	C3H4		81	Cl2	240-450	124	OSCl2	116-135
39	ClONO2	190-410	82	CL2O2	200-360	125	CH2N2	257-450
40	COF2	180-224	83	IBr	220-540	126	CH2CO	250-460
41	SF6		84	ICl	220-540	127	C3O2	110-320
42	CH2Cl2	160-250	85	CH3CHO	200-345			
43	CHCl3	160-250	86	Cl2O	200-500			

At present the UVACS contains data of absorption cross-sections of more than 120 substances in the spectral range from 106 to 720 nm. The collected data is based on more than 340 references. But it has to be noticed that the data are not still complete for many components.

However benefits of numerical calibration with the use of absorption cross-sections can be achieved only in the case if there are reliable and full data. In accordance with the BIPM recommendations e.g. result of measurement of gas concentration should have traceability to etalon and should have calculated uncertainty budget. Regular key comparisons of national etalons as well as comparisons of gas analyzers with the state etalons are made under aegis of the BIPM. Such way of work is used broadly and for a long time for big quantities of gaseous components including ozone. It being known that the standard reference photometer (SRP) is developed in USA as a reference for measurements of ozone concentrations using absorption cross-section of ozone at the absorption of 253.7 nm Hg Line.[2,3,4]

Unfortunately the use of the SRP as mechanism for measurement service delivery is more exception then a rule at present. The SRP is not included yet in a list of mechanisms for measurement service delivery.[2] Meanwhile work to conform the SRP as an etalon to ozone is going on in the BIPM with support of the NIST. This opportunity is studied in many countries, which signed Mutual Recognition Arrangement (MRA) BIPM including Russia. The BIPM and the NIST show the next uncertainty of measurements of ozone concentrations by the SRP[2,3]:

- 0 to 100 nmol/mol: +/- 1 nmol/mol
- 100 to 1000 nmol/mol: 1% relative

At the same time as it follows from the database of calibration and measurement capabilities (CMC) of the BIPM the other mechanism for measurement service delivery for ozone i.e. calibration by SRM gives worse values of uncertainty.[2]

One of the main problems to conform broadly numerical data of absorption cross-sections or line parameters to calibration of optical gas analyzers is low accuracy of available numerical data. Although absorption cross-section of ozone at 253.7 nm wavelength is defined rather accurate (ISO 13964:1998 gives expanded relative uncertainty at 1.5 % (k=2)) for other gaseous species absorption cross-sections or line parameters are defined with worse accuracy as a rule. It has to be noticed that for ozone the error estimates are not rigorous numbers resulting from a detailed error propagation analysis of statistical manipulations of the different sets of literature values; they merely represent a consensus among the panel members taking into account the difficulty of the measurements, the agreement among the results reported by various groups etc.[5]

The internationally recognized standard HITRAN database is updated routinely as well. There is established an advisory committee which reviews and evaluates new data. But nevertheless values of line parameters can vary greatly from the previous to the last HITRAN edition. For example updates were made in the last edition for the first overtone of $^{12}C^{16}O$ located near 2.4 µm. These new results show that the line intensities of the previous HITRAN edition[6] were systematically larger by 4.2% that those in the last version of the HITRAN[7], where the measured intensities were reported to be 1 to 6 % smaller than those reported in the previous HITRAN edition.[6] Similarly in the case of the second overtone (3-0) of $^{12}C^{16}O$ located around 1.6 µm, measured intensity values were smaller by 5-7%. Difference caused by air-broadening among the previous and updated HITRAN editions is substantial. Uncertainty indices of line position and intensity “Ierr” for CO in the spectral range where the following calculations were made also are still low. Hence orienting on foregoing uncertainties of the line intensities as well as on uncertainty indices presented in the HITRAN database and as an example of the HITRAN database use, change of signal of a gas-filter correlation (GFC) instrument depending on likely dispersion of line intensities can be estimated.

Algorithm of functioning and method of compensating for changes of any kind in spectra (method of spectral compensation) for GFC gas analyzer are described in previous works.[8,9]
A value of monochromator slit bandwidth at 0.5 peak transmittance is $\Delta\lambda(0.5) = 10\ cm^{-1}$. CO integral content in a reference cell of GFC analyzer is 1000 ppm m. All calculations were made for atmospheric pressure and 296 °K temperature. At first, there is chosen in the spectral range 2150-2200 cm^{-1} a wavelength λ=2171 cm^{-1} where is practically no water interference in broad range of changing of integral content of water vapor from 0 to 100,000 ppm m, and where good sensitivity for CO is achieved. So at this wavelength calibration of GFC analyzer is possible in presence of water vapor. Next, signal of a GFC instrument is calculated in the same spectral range 2150-2200 cm^{-1} using lines intensities taken from the HITRAN database for CO integral content CL=10 ppm m (fig.2), and then for a case of 95% lines intensities near λ=2171 cm^{-1} for the same CO integral content CL=10 ppm m (fig.3). A graph of GFC instrument signal change at λ=2171 cm^{-1} depending on change of lines intensities is presented on fig.4.

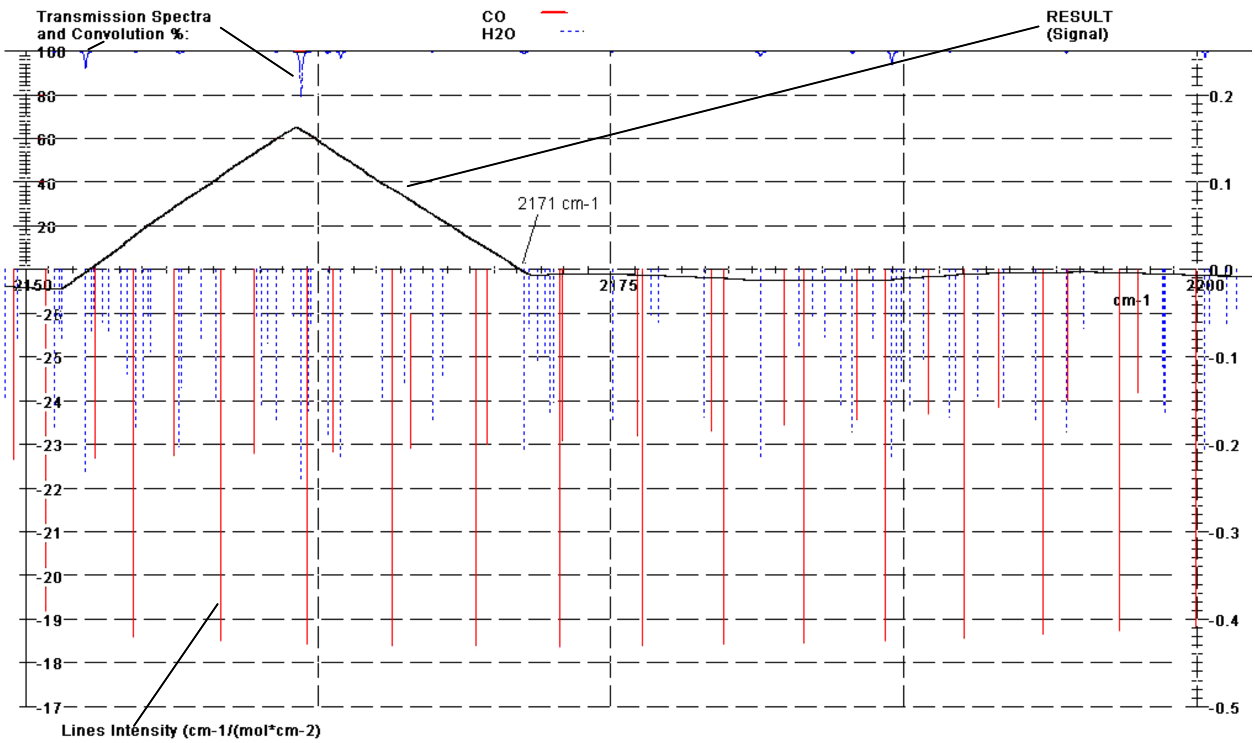

Fig. 1. H_2O interference. Change of water integral content from 0 to 100,000 ppm m, CO integral content CL=0, $\Delta\lambda(0.5)$=10 cm^{-1}. Signal of gas analyzer is zero at the wavelength near 2171 cm^{-1}.

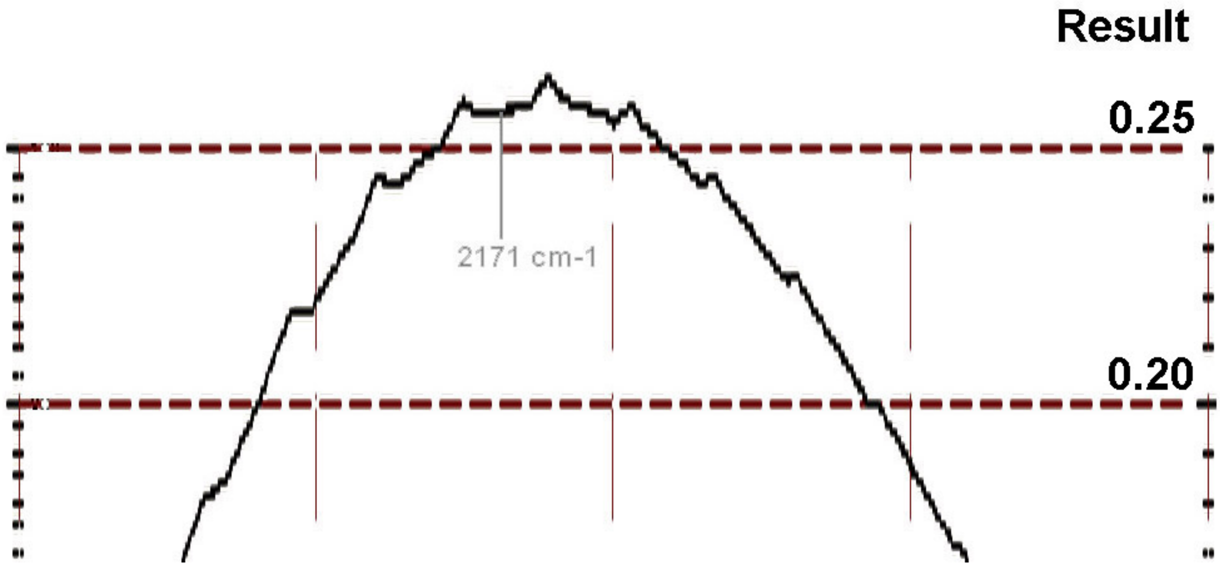

Fig. 2. Calculated curve illustrating the signal output for CO integral content CL=10 ppm m, $\Delta\lambda(0.5)$=10 cm^{-1} in the spectral range 2150-2200 cm^{-1} using lines intensities taken from the HITRAN database. Lines intensities used for calculation at λ=2169.1979 and λ=2172.7588 cm^{-1} are real i.e. 100% of nominal.

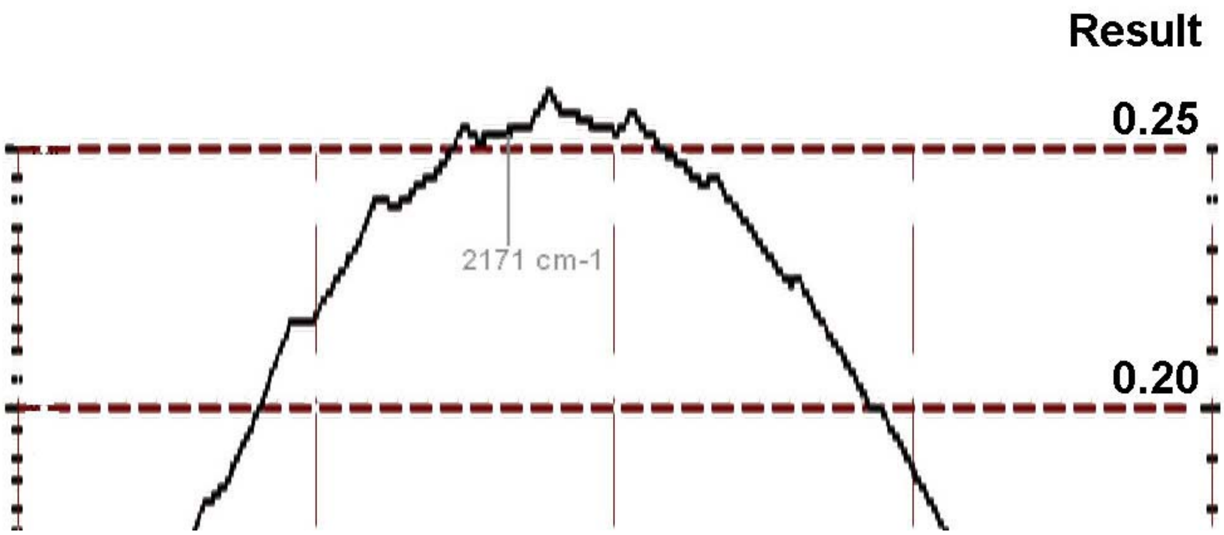

Fig. 3. Calculated curve illustrating the signal output for CO integral content CL=10 ppm m, $\Delta\lambda(0.5)$=10 cm^{-1} in the spectral range 2150-2200 cm^{-1} using lines intensities taken from the HITRAN database. Lines intensities used for calculation at wavelength λ=2169.1979 and λ=2172.7588 cm^{-1} are 95% of nominal.

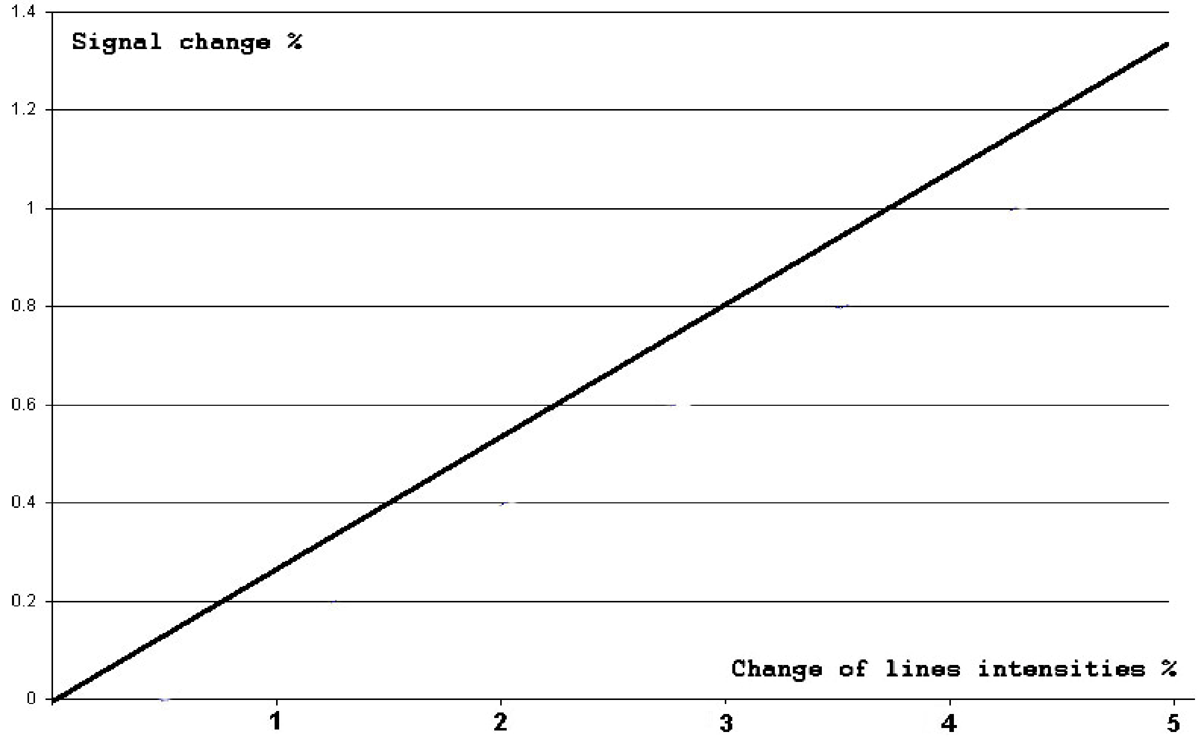

Fig. 4. Graph illustrating signal change of GFC instrument depending on change of lines intensities at wavelength λ=2171 cm^{-1}, $\Delta\lambda(0.5)$=10 cm^{-1}.

Proceeding from the assumption that lines intensities for CO are not defined precisely the foregoing graph could be extended in both directions. Output signal of GFC instrument can vary considerably and hence precise calibration of CO GFC analyzer by means of numerical parameters is impossible.

So there is need of more precise definition of absorption cross-sections or line parameters for tasks of calibration of analyzers. At that the problem arise to develop spectral procedure of measurement. Some algorithms are developed by now to precisely calculate absorption spectra taking into assumption instrumental parameters of FTIR instrument such as random noise in absorption spectra, inclination of base line of absorption spectra, base line level of absorption spectra, spectral shift in scale of wavenumbers, instrumental function.[10] However standardization of such measurement procedures is necessary. Yet , CMC of National Metrological Institutes (CMC NMI BIPM[2]) show that to give more precise definition to spectral constants it is expedient to use as internationally recognized SRMs as well as an experience of the BIPM.

Conclusions:

Assuming an experience of key comparisons NMI BIPM from one side and successful usage of spectral constant as an etalon for Ozone SRP the next conclusions can be made:

1. To achieve better accuracy the present format of collecting data from different scientists working with the use of different instrumentation should be changed.
2. Interaction of HITRAN, UVACS databases and CMC NMI BIPM database should be organized.
3. The use of internationally recognized SRM of CMC NMI BIPM database which includes more than 140 gas mixtures with a wide range of certified values in reference materials from 5 nmol/mol to 100% and with a range of expanded uncertainties from 0.1% to 5% and use of standard measurement procedures carried out with IR spectrophotometers with resolution better than 0.01 cm^{-1} and accuracy of transmittance better than 0.1% and also with UV spectrophotometers with resolution better than 0.05 nm and accuracy of transmittance better

than 0.1% may as we assume increase the accuracy of the HITRAN and the UVACS databases substantially.

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