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Enhanced environmental protection inspection for efficient control of air quality monitoring and of all entities under obligation within system of greenhouse gas emission allowance trading, in order to achieve better quality of air in Republic of Croatia

REPUBLIKA HRVATSKA
MINISTARSTVO ZAŠTITE OKOLIŠA I ENERGETIKE

EKONERG

safu SREDIŠNJA AGENCIJA ZA FINANCIRANJE I UGOVARANJE

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EKONERG Energy Research and Environmental Protection Institute

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THEME 6: QA/QC (quality assurance/quality control)

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6.1 TARGETED DATA QUALITY

According to ISO 8402, we can say that:

The quality - the totality of the characteristics of an entity that demonstrates its ability to comply with the stated or implied requirements and / or needs.

Targeted data quality - represents the legal minimum required for the quality of data obtained by air quality measurements in one year.

6.1 TARGETED DATA QUALITY

- Only data that can be used to document the target quality can be used to run any kind of legally prescribed procedures.

- Almost all measurements of air quality are determined by regulatory or inspection. Because of this, achieving and documenting the targeted quality of data sets as the primary goal of all QA / QC procedures in a network.

6.1 TARGETED DATA QUALITY

Targeted data quality

Parametar/onečišćujuća tvar	Sumporov dioksid, dušikov dioksid i oksidi dušika	Benzen	Ugljikov monoksid	Lebdeće čestice (PM10/PM2,5) i olovo	Ozon i pridruženi dušikovi oksidi: NO i NO2
Stalna mjerenja:[1] nesigurnost minimalan obuhvat podataka Minimalna vremenska pokrivenost (gradska, pozadinska, prometna)	15% 90% – –	25% 90% 35% [2] 90%	15% 90% – –	25% 90% – –	15% 90% ljeti 75% zimi – –
Indikativna mjerenja: [1A] nesigurnost minimalan obuhvat podataka minimalna vremenska pokrivenost	25% 90% 14% [4]	30% 90% 14% [3]	25% 90% 14% [4]	50% 90% 14% [4]	30% 90% > 10% ljeti

6.1 TARGETED DATA QUALITY

Targeted data quality (extension table)

Parametar/onečišćujuća tvar	Sumporov dioksid, dušikov dioksid i oksidi dušika	Benzen	Ugljikov monoksid	Lebdeće čestice (PM10/PM2,5) i olovo	Ozon i pridruženi dušikovi oksidi: NO i NO2
Nesigurnost modeliranja:					
satna	50%	–	–	–	–
8-satni prosjeci	–	–	50%	–	–
dnevni prosjeci	50%	–	–	nije definirano	50%
godišnji prosjeci	30%	50%	–	50%	50%
Objektivna procjena: nesigurnost	75%	100%	75%	100%	75%

6.2 QA/QC PLAN NETWORK

QA/QC plan network is the basic document on quality assurance of measurements in each network. It contains all the basic information on how quality assurance network is organized. QA/QC plan should have the following structure:

1. UVOD Svrha Opseg
2. REFERENTNI DOKUMENTI Zakonska regulativa Normativna regulativa
3. CILJANA KVALITETA PODATAKA
4. DIZAJN MREŽE 4.1 Onečišćujuće tvari koje se prate Kriteriji i dokumentacija za određivanje lokacija mjernih postaja Lokacije postaja 4.2 Oprema i mjerne metode Mjerna oprema – certifikati o tipskim odobrenjima QA/QC oprema 4.3 Mjerne metode 4.5 Organizacijska shema Organizacijske jedinice i njihove funkcije

6.2 QA/QC PLAN NETWORK

Extension table

5. POSTUPCI OSIGURANJA I KONTROLE KVALITETE
Postupci preventivnog održavanja
Postupci kontrole kvalitete na postaji
6. MJERNA NESIGURNOST
Sastavnice sastavljene mjerne nesigurnosti
Izračun mjerne nesigurnosti na razini GV-a
7. IZVJEŠĆA O MJERENJIMA
Ratifikacijska izvješća
Godišnje izvješće

6.2 QA/QC PLAN NETWORK

Below I will briefly discuss all the chapters that should include a QA / QC plan with special emphasis on the section on quality assurance and quality assurance procedures.

1. INTRODUCTION

In the introduction it is necessary to mention the importance of quality assurance and briefly define the purpose and scope of the document. It is also necessary to specify the basic goals of the network, as well as the reasons for its establishment.

6.2 QA/QC PLAN NETWORK

2. REFERENCE DOCUMENTS

This is an extremely important chapter. It should contain all reference documents that are referred to in the plan and which regulate and normatively define the operation of the network. By referring to legally or normatively defined methods of metering, and their consistent implementation and documenting, we ensure not only compliance but also disable the often malicious attempts to undermine the quality assurance of measurement. This also ensures the results of measurements that can be in practice and which are not acceptable to some.

6.2 QA/QC PLAN NETWORK

The Croatian regulation is almost fully harmonized with the European one. However, some of the guidelines issued by various environmental bodies in the EU can be of great help in defining QA / QC procedures.

Regulations Of The REPUBLIC Of CROATIA

- The law on air protection (Official Gazette, no. 130/11, 47/14, 61/17)
- Rulebook on monitoring air quality (Official Gazette 79/17)
- Ordinance on the mutual exchange of information and the reporting of air quality and commitments for the implementation of the decisions of the Commission 2011/850/EU (Official Gazette 3/16)
- The regulation on the levels of pollutants in the air (OFFICIAL GAZETTE 117/12)

6.2 QA/QC PLAN NETWORK

Regulations and guidelines of the EU

- Directive 2008/50/EC of the European Parliament and of the Council
- Commission Directive (EU) 2015/1480
- Implementing the Commission's decision of 12. December 2011. laying down rules for Directive 2004/107/EC and 2008/50/EC of the European Parliament and of the Council concerning the mutual exchange of information and reporting on the quality of the air (2011/850/EU)
- Guidance on the Decision 2011/850/EU
- „Criteria for EUROAIRNET The EEA Air Quality Monitoring and Information Network“; EEA Technical Report No. 12
- “QA/QC checks on air quality data in AIRBASE and on the EoI 2004 data Procedures and results”; ETC/ACC Technical paper 2005/3 September 2005; Wim Mol and Patrick van Hooydonk

6.2 QA/QC PLAN NETWORK

When referring to the normative regulation in the QA / QC plan, it is necessary to state the general normative acts under which the measurements are carried out and to note that specific norms are mentioned in the lower quality assurance documents. The most important general normative acts relevant to quality assurance in the area of air quality are:

- **HRN EN ISO / IEC 17025 - General requirements for the qualification of testing and calibration laboratories**
- **ENV 13005, Guide to the expression of uncertainty in**
- **measurement**
- **EN ISO 14956:2002 Air quality. Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty.**

6.2 QA/QC PLAN NETWORK

3. TARGETED DATA QUALITY

It is necessary to mention the target quality data set for the pollutant and the types of measurement / modeling that are implemented in the network.

4. NETWORK DESIGN

In this chapter it is necessary to specify in detail how the network is designed. When writing this chapter that refers to points 4.1 to 4.3 QA/QC plan should respect the provisions of the regulations on the exchange of information about the data from the network for permanent monitoring of air quality (OFFICIAL GAZETTE 135/06) which defines the so-called metadata about the network, and each individual station.

6.2 QA/QC PLAN NETWORK

5. QUALITY INSURANCE CONTROL

The primary goal of QA / QC procedures is to ensure targeted data quality and provide documentation that will document it. The quality system shall be written in accordance with the provisions of the EN ISO / IEC 17025 – General requirements for the competence of testing and calibration laboratories and certain prescribed measurement methods standards. Although each network has its own specifics, insurance and quality control for automatic measurements typically consists of the below described procedures.

6.2 QA/QC PLAN NETWORK

Preventive maintenance procedures

Preventive maintenance of instruments is based on measurement methods, equipment manufacturer recommendations and experience. Typically consists of:

- regular status verification of the instrument's technical validity
- regular service and checking of the station
- regular maintenance of the system for sampling
- the regular annual services.

6.2 QA/QC PLAN NETWORK

Quality control procedures at the stations

Quality control procedures on the station should be designed on the basis of the norms of the measurement methods, the recommendations of the manufacturer of the equipment and the experience. These procedures are used primarily to control the daily work of the instruments, or the total of the measuring system. This gives regular insight into the functionality of the instruments and enables a timely reaction to irregularities in the work of instruments that could otherwise remain unnoticed for a long time.

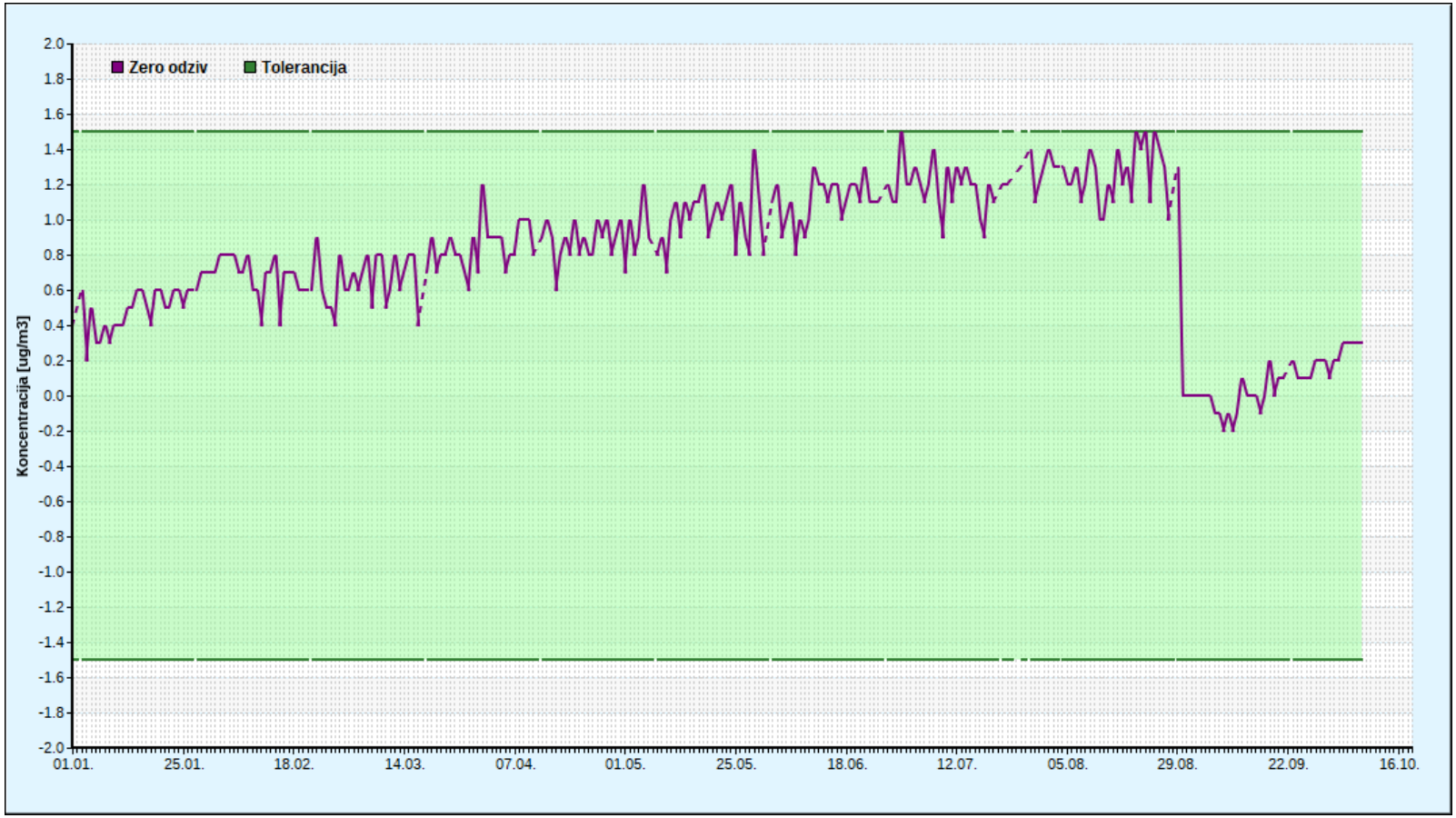
6.2 QA/QC PLAN NETWORK

Quality control procedures at the stations usually consist of:

- **checking the response og the zero gas "ZERO CHECKING„**
- **checking the response of the calibration gas "SPAN CHECKING„**
- **calibration at two points**
- **recertification of gases**
- **testing of the sampling line**
- **testing of the sampler manifolds.**

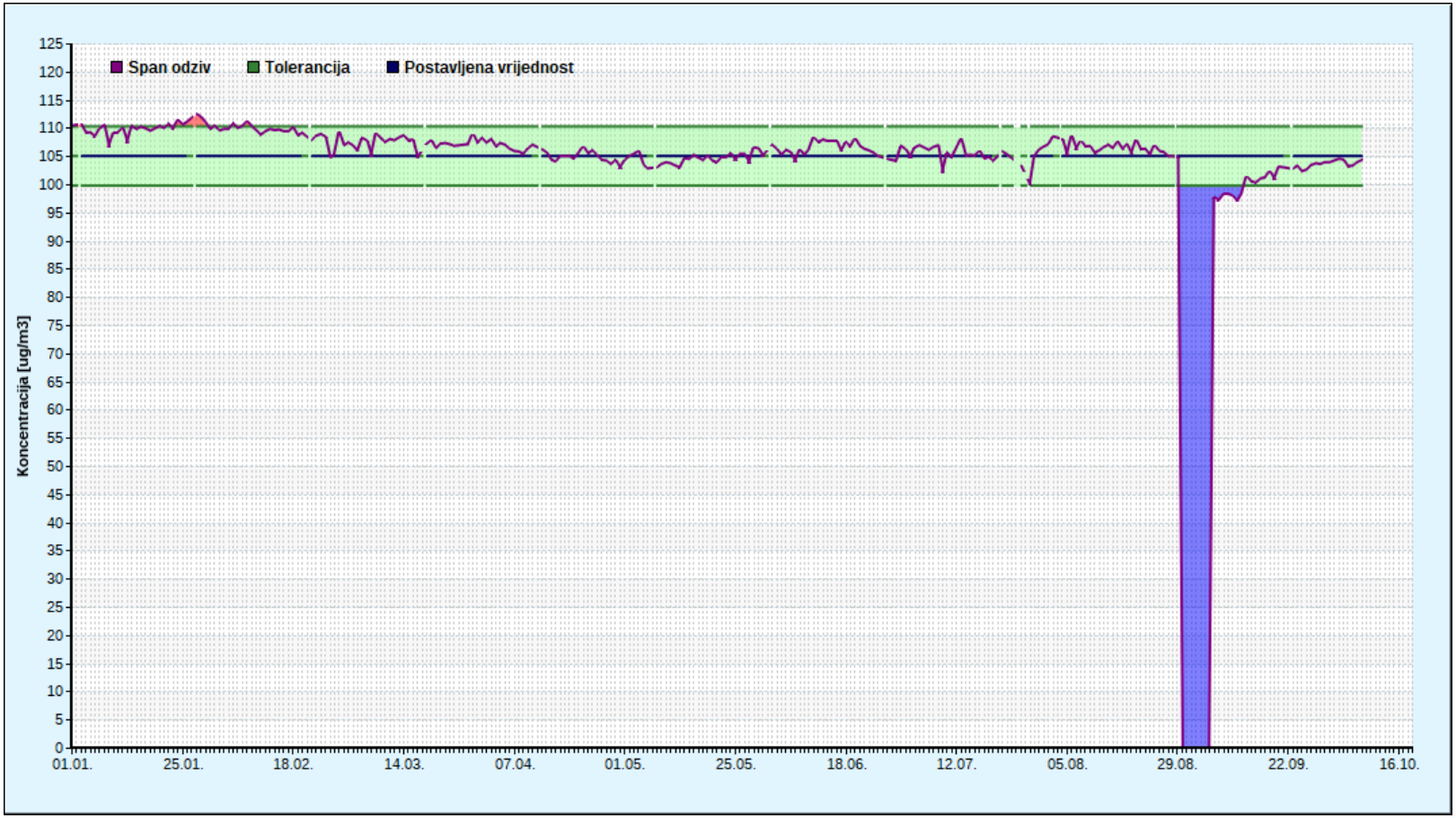
6.2 QA/QC PLAN NETWORK

Quality control procedures at the stations



6.2 QA/QC PLAN NETWORK

Quality control procedures at the stations



6.2 QA/QC PLAN NETWORK

Calibration and tests in the laboratory

After each annual service or after major servicing of the instrument the calibration and testing of the instrument is performed in a calibration laboratory. Such tests, as well as, quality control data in the station together with the data obtained during the performance of the type approval tests are used to calculate the measurement uncertainty that is being carried out each year. Operating performance tests are designed based on standardized metering methods. Also for the conducted tests, in the standards for certain methods, the acceptable limits have to be met.

6.2 QA/QC PLAN NETWORK

Such procedures typically consist of:

- **calibration with certified or primary standards**
- **"lack of fit" test in three or four points and zero gas**
- **testing of repeatability standard deviation**
- **testing of short-term offset**

6.2 QA/QC PLAN NETWORK

For the purpose of quality assurance and quality control, documentation is developed which describes the procedures and establishes documents that document the regular conduct of the procedures.

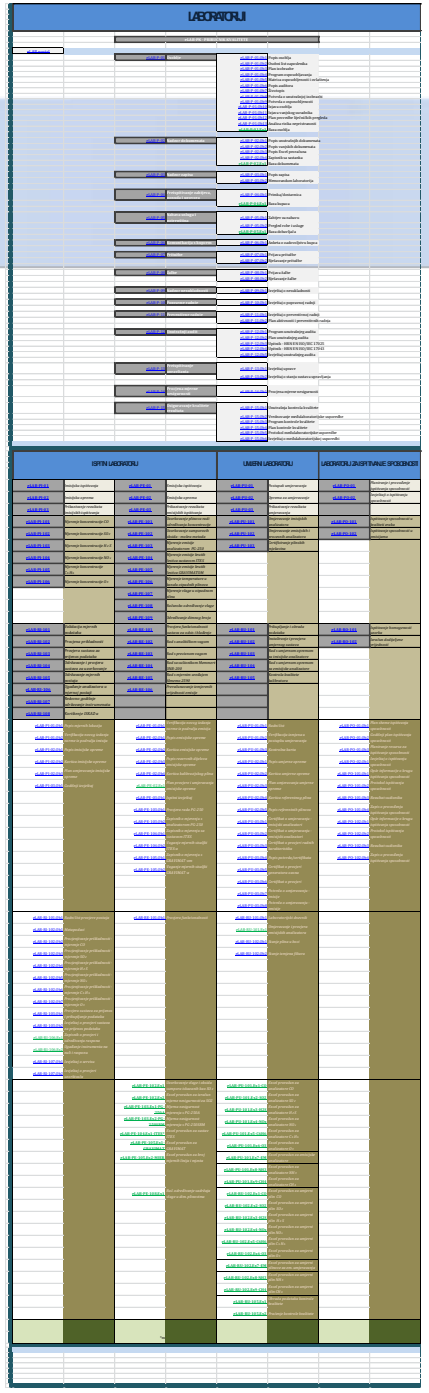
Performing procedures should ensure the proper functioning of the equipment both in the technical and in the analytical sense, enable the prediction of possible problems and their avoidance or elimination as soon as possible.

All completed procedures need to be well documented and kept in line with the legal and normative regulations.

DOCUMENTATION

6.2 QA/QC PLAN NETWORK

ISPITNI LABORATORIJ			
eLAB-PI-01	*Imisijska ispitivanja*	eLAB-PE-01	*Emisijska ispitivanja*
eLAB-PI-02	*Imisijska oprema*	eLAB-PE-02	*Emisijska oprema*
eLAB-PI-03	*Prikazivanje rezultata imisijskih ispitivanja*	eLAB-PE-03	*Prikazivanje rezultata emisijskih ispitivanja*
eLAB-PI-101	*Mjerenje koncentracije CO*	eLAB-PE-101	*Uzorkovanje plinova radi određivanja koncentracije*
eLAB-PI-102	*Mjerenje koncentracije SO_2*	eLAB-PE-102	*Uzorkovanje sumporovih oksida - mokra metoda*
eLAB-PI-103	*Mjerenje koncentracije H_2S*	eLAB-PE-103	*Mjerenje emisije analizatorom PG-250*
eLAB-PI-104	*Mjerenje koncentracije NO_x*	eLAB-PE-104	*Mjerenje emisije krutih čestica sustavom ITES*
eLAB-PI-105	*Mjerenje koncentracije C_6H_6*	eLAB-PE-105	*Mjerenje emisije krutih čestica GRAVIMATOM*
eLAB-PI-106	*Mjerenje koncentracije O_3*	eLAB-PE-106	*Mjerenje temperature u kanalu otpadnih plinova*
		eLAB-PE-107	*Mjerenje vlage u otpadnom plinu*
		eLAB-PE-108	*Računsko određivanje vlage*
		eLAB-PE-109	*Određivanje dimnog broja*
eLAB-RI-101	*Validacija mjernih podataka*	eLAB-RE-101	*Provjera funkcionalnosti sustava za odsis i hlađenje*
eLAB-RI-102	*Procjena prikladnosti*	eLAB-RE-102	*Rad s analitičkom vagom*
eLAB-RI-103	*Provjera sustava za prijenos podataka*	eLAB-RE-103	*Rad s preciznom vagom*
eLAB-RI-104	*Održavanje i provjera sustava za uzorkovanje*	eLAB-RE-104	*Rad sa sušionikom Memmert UNB-200*
eLAB-RI-105	*Održavanje mjernih postaja*	eLAB-RE-105	*Rad s mjernim uređajem Almemo 2590*
eLAB-RI-106	*Ugađanje analizatora u mjernoj postaji*	eLAB-RE-106	*Preračunavanje izmjerenih vrijednosti emisije*
eLAB-RI-107	*Redovno godišnje održavanje instrumenata*		
eLAB-RI-108	*Korištenje ISKAZ-a*		



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6.2 QA/QC PLAN NETWORK

6. MEASUREMENT UNCERTAINTY

Based on the data from the type approval, laboratory tests and station tests, the parameters are calculated as follows:

- the measurement uncertainty for the data from the period to be reported in the annual report in the form of an expanded uncertainty of uncertainty for the lowest defined averaging time at the Uc limit value
- absolute expanded measurement uncertainty for averaging time at the limit value Uc
- relative measurement uncertainty Uc (relative measurement uncertainty should be expressed for each individual instrument in the network.)

6.2 QA/QC PLAN NETWORK

MEASUREMENT UNCERTAINTY

$$u_c = \sqrt{(u_{r,z})^2+(u_{r,l/v})^2+(u_l)^2+(u_{gp})^2+(u_{gt})^2+(u_{st})^2+(u_V)^2+(u_{H2O})^2+(u_{int})^2+(u_{av})^2+(u_{dl,z})^2+(u_{dl,l/v})^2+(u_{cg})^2}$$

$$U_c = k \times u_c \quad (k=2)$$

$$U_{c,rel} = (U_c/\text{hlv}) \times 100$$

PROCJENA MJERNE NESIGURNOSTI na razini GV za APMA-370 analizatore

Mjerna nesigurnost na razini GV za **APMA 370 ZAJ**

Mjerna postaja /

				Testovi obavljeni	9.9.2017.
Br. testa iz EN 14626	**Oznaka iz EN 14626**	**Standardna mjerna nesigurnost zbog…**	**Rezultati iz testova RK**	**u (p) (µmol/mol)**	**$u^2(p)$**
1	($u_{r,z}$)	ponovljivosti na zero plinu	134/2017	0,0010	0,0000
2	($u_{r,l/v}$)	ponovljivosti na graničnoj vrijednosti za 8 h GV*	134/2017	0,0007	
3a	(u_l)	Lack of fit test za 8 h GV	134/2017	0,0271	0,0007
4	(u_{gp})	utjecaja varijabilnosti tlaka uzorkovanog plina	Tip. odobrenje Tablica 38	0,012	0,0001
5	(u_{gt})	utjecaja varijabilnosti temperature uzorkovanog plina	Tip. odobrenje Tablica 38	0,024	0,0006
6	(u_{st})	utjecaja varijabilnosti temperature okolnog zraka	Tip. odobrenje Tablica 38	-0,1823	0,0332
7	(u_V)	utjecaja varijabilnosti napona el. struje	Tip. odobrenje Tablica 38	0,028	0,0008
8a	(u_{H2O})	prisutnosti vodene pare na graničnoj vrijednosti za 8 h GV	Tip. odobrenje Tablica 38	0,3261	0,1063
8b,c,d	(u_{int})	Interferirajućih tvari (pozitivna int. – negativna int.)	Tip. odobrenje Tablica 38	0,4051	0,1641
9	(u_{av})	efekta usrednjavanja	Tip. odobrenje Tablica 38	0,0621	0,0039
10	(u_{rl})	reproducibilnost*	Tip. odobrenje Tablica 38	0,0052	0,00003
11	($u_{dl,z}$)	dugotrajnog pomaka na zero plinu	Tip. odobrenje Tablica 38	0,0993	0,0099
12	($u_{dl,l/v}$)	dugotrajnog pomaka na graničnoj vrijednosti za 8 h GV	Tip. odobrenje Tablica 38	0,0268	0,0007
21	(u_{cg})	kalibracijskog plina na 8 h GV	134/2017	0,1592	0,0253
Kvadrat složene mjerne nesigurnosti $u^2 = \sum u^2(p)$					**0,35**
Složena mjerna nesigurnost na 8 h GV $u_{GV} = \sqrt{u^2}$ (µmol/mol)					0,59
Proširena mjerna nesigurnost na 8 h GV $U_{GV} = u*k$ (k=2) (µmol/mol)					1,18
Relativna mjerna nesigurnost na 8 h GV $U_{GV,rel} = (U_{GV}/8,6)*100$ (%)					13,67
Regulatorno tražena relativna mjerna nesigurnost na 8 h GV (%)					**15**

** uzeta reproducibilnost jer je veća od ponovljivosti*

ZAKLJUČAK	Kvaliteta mjerenja s obzirom na ciljanu kvalitetu mjerenja -	zadovoljava

DATUM	IZRADIO
9.9.2017.	/

eLAB-PI-101.Ex1/1

6.2 QA/QC PLAN NETWORK

Measurement uncertainty is calculated in accordance with ENV 13005, Guide to the expresion of uncartainity in measurement i EN ISO 14956:2002 Air quality, Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty and CEN standards for individual pollutants.

7. Measurement reports

The laboratory that performs measurements in a particular network over the year informs the network coordinator through the ratification reports about the network operation and the measurement results. Likewise, at the end of the one-year measurement period set by regulation, the laboratory appends an annual report

6.2 QA/QC PLAN NETWORK

Ratification Report

The Ratification Report is a periodic report in which the laboratory reports to the coordinator or network owner on all aspects of network operation and ratifies the measurement data for a specific period. Such reports are usually produced for a period of one to three months, depending on the requirements of the network owner. They are not obligatory and they are a matter of contract.

Yearly report

It is produced after the end of a one-year period.

6.3 MEASUREMENT TRACEABILITY AND CALIBRATION LABORATORY

Automatic instruments for monitoring the air quality require strict quality control of measurements. One of the most important quality assurance procedures is regularly calibration and testing of the instruments. The calibration is done at the stations and in the calibration laboratories. Calibration laboratory should ensure and document the accuracy and traceability of the measuring data and allow for the expression of measurement uncertainty at the level of the limit values for each instrument in the network. Only with the good cooperation of the testing and the calibration laboratories (with the support of the service team) can reach the extremely challenging regulatory target the quality of the data.

6.3 MEASUREMENT TRACEABILITY AND CALIBRATION LABORATORY

The calibration of instruments and measurement traceability

The calibration of the instruments is carried out periodically. CEN-standards require calibration of instruments at stations every three months. This procedure is performed with the help of a certified gas cylinders (CRM certified referent material CRM) at two points (zero and the so-called span which represents a concentration of 70 to 80% of the maximum certified measurement range) which ensures traceability.

It is also necessary to perform calibration in the laboratory after each major instrument intervention (major repairs, annual service). This is followed by testing performance of the instrument required by the same standards.

6.3 MEASUREMENT TRACEABILITY AND CALIBRATION LABORATORY

The most common and the most useful tests are so called. "LACK OF FIT" test (which represents the linearity test and is most often performed in 5 points within the measurement range), "STANDARD DEVIATIONS REPEATABILITY" test (which checks the repeatability of the instrument) and "SHORT TERM DRIFT" test which checks the stability of the measurements in a short period. If the instrument after the calibration meets the standard prescribed criteria for the above tests and if the calibration is ensured traceability, the prepared instrument is ready for measurements at the station. Calibration in laboratories is also carried out with the help of traceable reference materials.

6.3 MEASUREMENT TRACEABILITY AND CALIBRATION LABORATORY

"lack of fit" test in three or four points and zero gas

IZRAČUN NELINEARNOSTI

1. Zadane koncentracije

% mjernog područja	$c(CO)_{an}$	$c(CO)_{ref}$
0	0,01	0,00
20	17,27	17,20
60	51,79	51,90
80	68,35	68,30
95	81,00	81,80

2. Izračun A i B

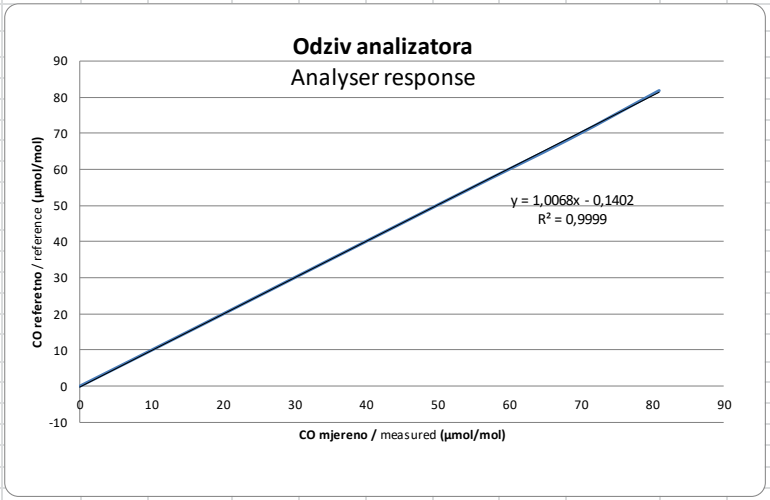
Yi = A + B * Xi	
B =	1,0068
A =	-0,1402

3. Izračun regresijskih odstupanja

(Ya)c	A+Bc	rc	rc,rel	ABS
0,01	-0,13	0,13	N/A	
17,27	17,25	-0,05	-0,29%	0,29%
51,79	52,00	-0,10	-0,19%	0,19%
68,35	68,67	-0,37	-0,55%	0,55%
81,00	81,41	0,39	0,48%	0,48%

4. Odstupanja

najveće odstupanje X_i=	0,55%	%
odstupanje na nuli $X_{i,z}$=	0,13	ppm



5. Izračun standardne mj. nesigurnost na satnoj graničnoj vrijednosti

HRN EN 14626:2012

jednadžba E.11 $u_{l,lh} = \frac{r_{max}}{100} \cdot \frac{l_h}{\sqrt{3}}$

parametar	vrijednost
r_{max}	0,55%
8lh=	8,6
$u_{l,lv}$	0,027

6.3 MEASUREMENT TRACEABILITY AND CALIBRATION LABORATORY

standard deviation repeatability test

PONOVLJIVOST na nultom plinu i koncentraciji raspona

STANDARDNO ODSTUPANJE PONOVLJIVOSTI

	x_i (ppm)					x_i (ppm)
	CO (20%)	CO (60%)	CO (span)	CO (95%)		CO (0%)
broj mjerenja	17,2	51,9	68,3	81,8	*broj mjerenja*	0
1	17,3	51,8	68,4	80,99	1	0,0
2	17,3	51,8	68,4	80,97	2	0,0
3	17,3	51,8	68,4	80,98	3	0,0
4	17,3	51,8	68,3	80,99	4	0,0
5	17,3	51,8	68,3	81,03	5	0,0
6	17,3	51,8	68,4	80,98	6	0,0
7	17,3	51,8	68,4	80,98	7	0,0
8	17,3	51,8	68,3	81,02	8	0,0
9	17,3	51,8	68,3	81,01	9	0,0
10	17,3	51,8	68,4	81,02	10	0,0
11	17,3	51,8	68,4		11	0,0
12	17,3	51,8	68,3		12	0,0
13	17,3	51,8	68,3		13	0,0
14	17,3	51,8	68,3		14	0,0
15	17,3	51,8	68,3		15	0,0
16	17,3	51,8	68,3		16	0,0
17	17,3	51,8	68,3		17	0,0
18	17,3	51,8	68,3		18	0,0
19	17,3	51,8	68,3		19	0,0
20	17,3	52,0	68,3		20	0,0
avg	17,27	51,80	68,34	81,00	avg	0,00
SD	0,009	0,048	0,021	0,023	SD	0,004
RSD	0,05%	0,09%	0,03%	0,03%		

MJERNA NESIGURNOST ZBOG PONOVLJIVOSTI

1. nesigurnosti zbog ponovljivosti analizatora

$$u_{r,i} = \frac{s_{r,i}}{\sqrt{n}}$$

u_r - nesigurnost zbog ponovljivosti
sr - ponovljivost
n - broj mjerenja
i - točka mjerenja (s-span; z-nula)

0	17,2	51,9	68,3	81,8
0,001	0,002	0,011	0,005	0,007

$u_{r,s}$ =	0,00459
$u_{r,z}$ =	0,00091
$u_{r,20\%}$ =	0,00200

2. nesigurnosti zbog ponovljivosti koje se izražavaju u godišnjem izvješću

HRN EN 14626:2012

$u_{r,lh} = \frac{s_{r,lh}}{\sqrt{m}}$ *kod satne granične vrijednosti (ppm)*

$u_{r,z} = \frac{s_{r,z}}{\sqrt{m}}$ *kod nule (ppm)*

6.3 MEASUREMENT TRACEABILITY AND CALIBRATION LABORATORY

A national reference laboratory is required to ensure traceability of measurement for devices for automatic monitoring of air quality in the State network. (2008/50/EC Art. 3 Ann. AND C)

The traceability to the SI standard is achieved by the use of:

- **the primary standard gases (PRM) or gases certified in accredited laboratories (CRM)**
- **calibration of calibrators in the accredited laboratories**
- **regular proficiency testing with reference laboratory instruments organized by JRC (Ref. Lab EU) - WHO - AQUILA**

6.3 MEASUREMENT TRACEABILITY AND CALIBRATION LABORATORY

Several prominent institutions from which Croatian reference laboratory provide measuring traceability:

ČMI	**Brno**
NMI	**Delft**
Linde	**Prag**
UBA	**Beč**
NPL	**London**
LNI	**Geneve**
FMI	**Helsinki**

6.3 MEASUREMENT TRACEABILITY AND CALIBRATION LABORATORY

calibration with certified or primary standards

EKONERG • Umjerni laboratorij • Koranska 5, HR-10000 Zagreb
Tel: +385 (0)1 6000-111; Faks: +385 (0)1 6171-560

POPIS REFERENTNIH PLINOVA

IMISIJE	Stanje: 2017-07-03

	Plin	Oznaka	Broj boce	Broj certifikata	Valjanost certifikata (do)	Koncentracija u boci (%vol/ppm/ppb)	Mjerna nesigurnost (%vol/ppm/ppb)
1.	CO	RPI-CO/14128	8140862	Linde, 34/17	2018-02-09	14128 ppm	58 ppm
2.	SO_2	RPI-SO2/-100.4	8157894	Linde, 258/16	2017-12-14	100,38 ppm	0,94 ppm
3.	NO	RPI-NO/199.5	8141331	Linde, 31/17	2018-02-09	199,5 ppm	3,2 ppm
4.	H_2S	RPI-H2S/100.0	NG646	NPL, 2016020330	2018-04-14	100,1 ppm	1,1 ppm
5.	BTX	RPI-BTX/12.14	D090592	NPL, 2015010056	2017-03-13	12,14 ppm	0,24 ppm
6.	C_6H_6	RPI-C6H6/9.15	D834760	OMSZ, 188/2015	2016-11-10	9,15 ppm	0,36 ppm
7.	BTX	RPI-BTX/1.4	A4103	OMSZ, 128/2017	2018-06-01	1,38 ppm	0,075 ppm
8.	BTX	RPI-BTX/12	9690D	OMSZ, 129/2017	2018-06-06	14,37 ppb	0,78 ppb
9.	CH_4	RPI-CH4/10000	245306	BOC, 2573499	2020-03-05	10300 ppm	206 ppm
10.	NH_3	RPI-NH3/330	245303	BOC, 2574341	2017-03-31	330 ppm	6,6 ppm

6.3 MEASUREMENT TRACEABILITY AND CALIBRATION LABORATORY

calibration with certified or primary standards

THE LINDE GROUP

Linde

ilac-MRA

K 2316

Linde Gas a.s.
Specialty Gases Laboratory
Accreditation ČIA No. 2316
for Gas Mixtures
(ČSN EN ISO/IEC 17025:2005)
U Technoplynu 1324
198 00 Praha 9
tel.: +420 272 100 223

Certificate of Analysis No. 258/16

Customer: Linde Gas a.s.
U Technoplynu 1324
198 00 Praha 9

Commission: 103000443107

Gas mixture SO_2, balance N2

Cylinder AL 10l

Cylinder No. 8157894

Traceability traceability of the measurement is accomplished by comparation to primary gravimetric standard ČMI and is expressed as mol/mol.

Measurement results

Component	Nominal value (mol/mol)	Uncertainty (1) (mol/mol)	Measurement Method	Identification of CRM
SO_2	0,00010038	0,00000094	PP4.01.004	80027/99/16

(1) The reported expanded uncertainty of measurement is stated as the standard uncertainty of measurement multiplied by the coverage factor k=2 which for a normal distribution corresponds to a coverage probability of approximately 95 %.
The standard uncertainty of measurement has been determined in accordance with Dokument EA 4/02.

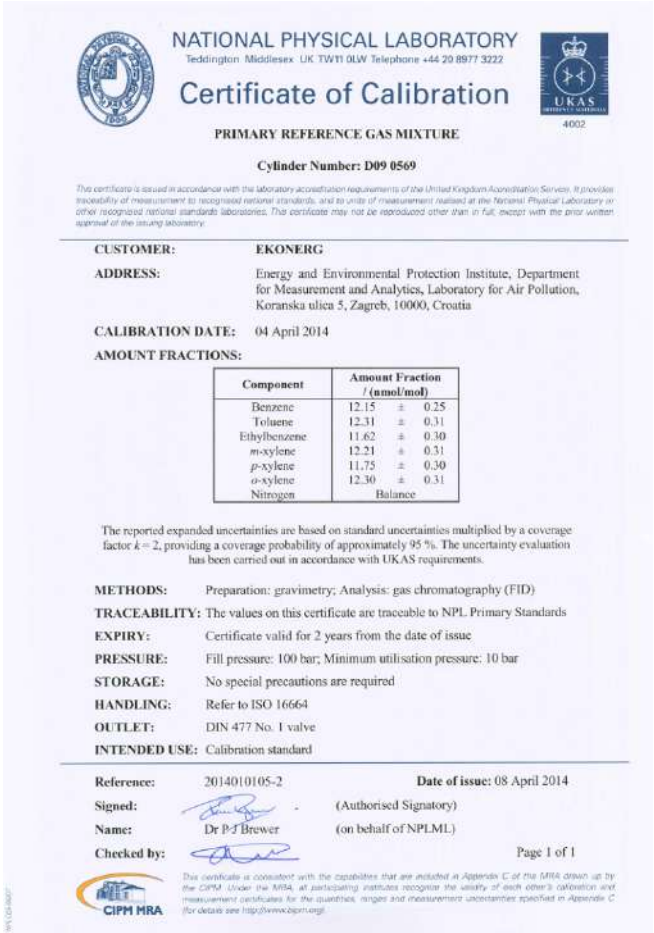
Date of receipt of calibration item: 2.12.2016
Laboratory temperature: (24 ± 4)°C
Measuring date: 5.12.2016
Measured by: Ing.Šmejkal
Date of authorisation: 15.12.2016

Ing. Jan Šmejkal
Senior manager of laboratory
Signature:

Linde Gas a.s.
Laborator specialních plynů
U Technoplynu 1324
198 00 Praha 9
Linde

This certificate is allowed to be published complete only.

Form 2444/3 A 2007.08 Page 1 of 1



NATIONAL PHYSICAL LABORATORY
Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

UKAS
4002

Certificate of Calibration

PRIMARY REFERENCE GAS MIXTURE

Cylinder Number: D09 0569

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to recognised national standards, and to units of measurement realised at the National Physical Laboratory or other recognised national standards laboratories. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

CUSTOMER: EKONERG

ADDRESS: Energy and Environmental Protection Institute, Department for Measurement and Analytics, Laboratory for Air Pollution, Koranska ulica 5, Zagreb, 10000, Croatia

CALIBRATION DATE: 04 April 2014

AMOUNT FRACTIONS:

Component	Amount Fraction / (nmol/mol)
Benzene	12.15 ± 0.25
Toluene	12.31 ± 0.31
Ethylbenzene	11.62 ± 0.30
m-xylene	12.21 ± 0.31
p-xylene	11.75 ± 0.30
o-xylene	12.30 ± 0.31
Nitrogen	Balance

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 2 years from the date of issue

PRESSURE: Fill pressure: 100 bar; Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No. 1 valve

INTENDED USE: Calibration standard

Reference: 20140101O5-2 **Date of issue:** 08 April 2014

Signed: (Authorised Signatory)

Name: Dr P J Brewer (on behalf of NPLML)

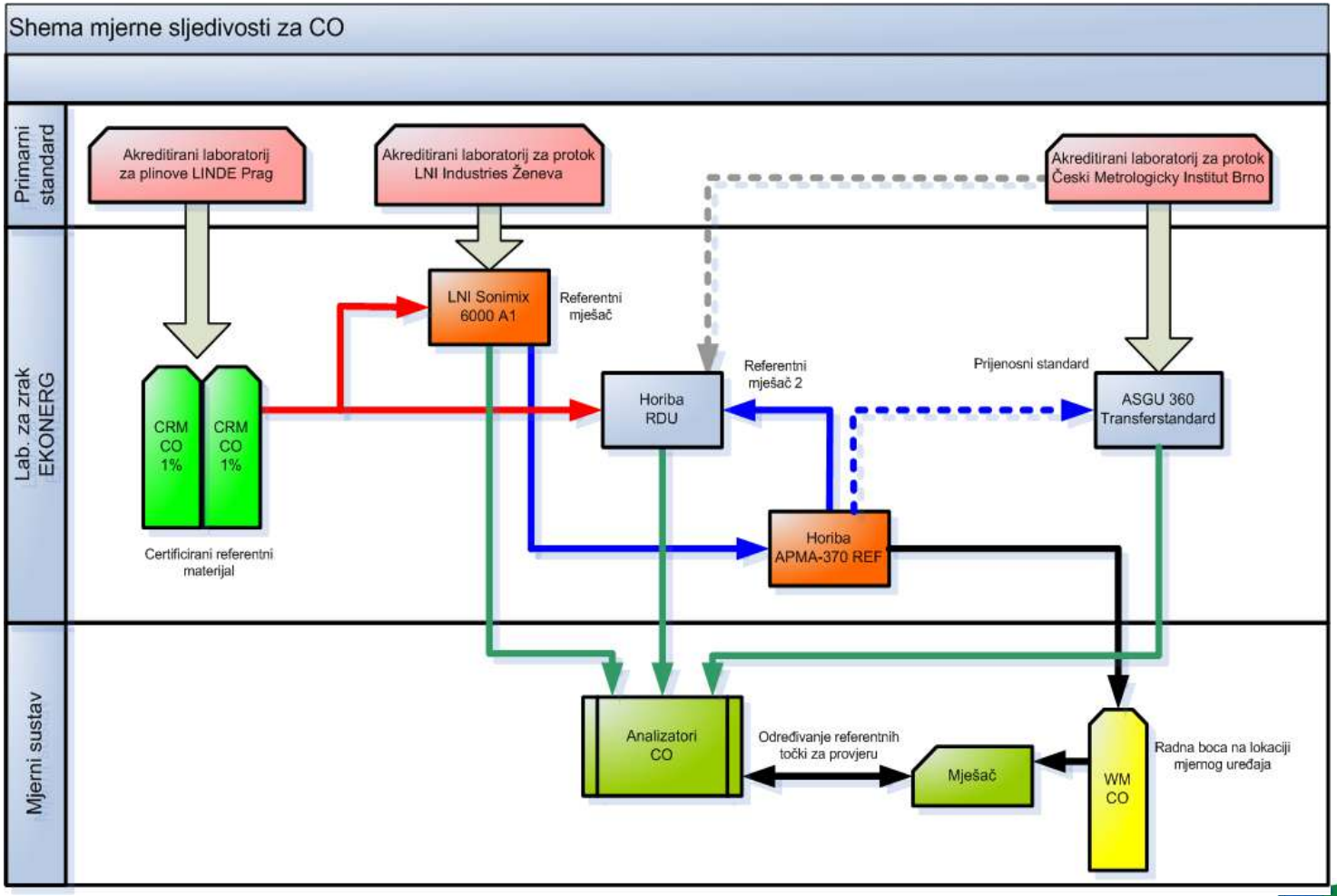
Checked by:

Page 1 of 1

CIPM MRA

This certificate is consistent with the capabilities that are included in Appendix C of the MRA drawn up by the CIPM. Under the MRA, all participating institutes recognise the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (for details see http://www.bipm.org).

6.3 MEASUREMENT TRACEABILITY AND CALIBRATION LABORATORY



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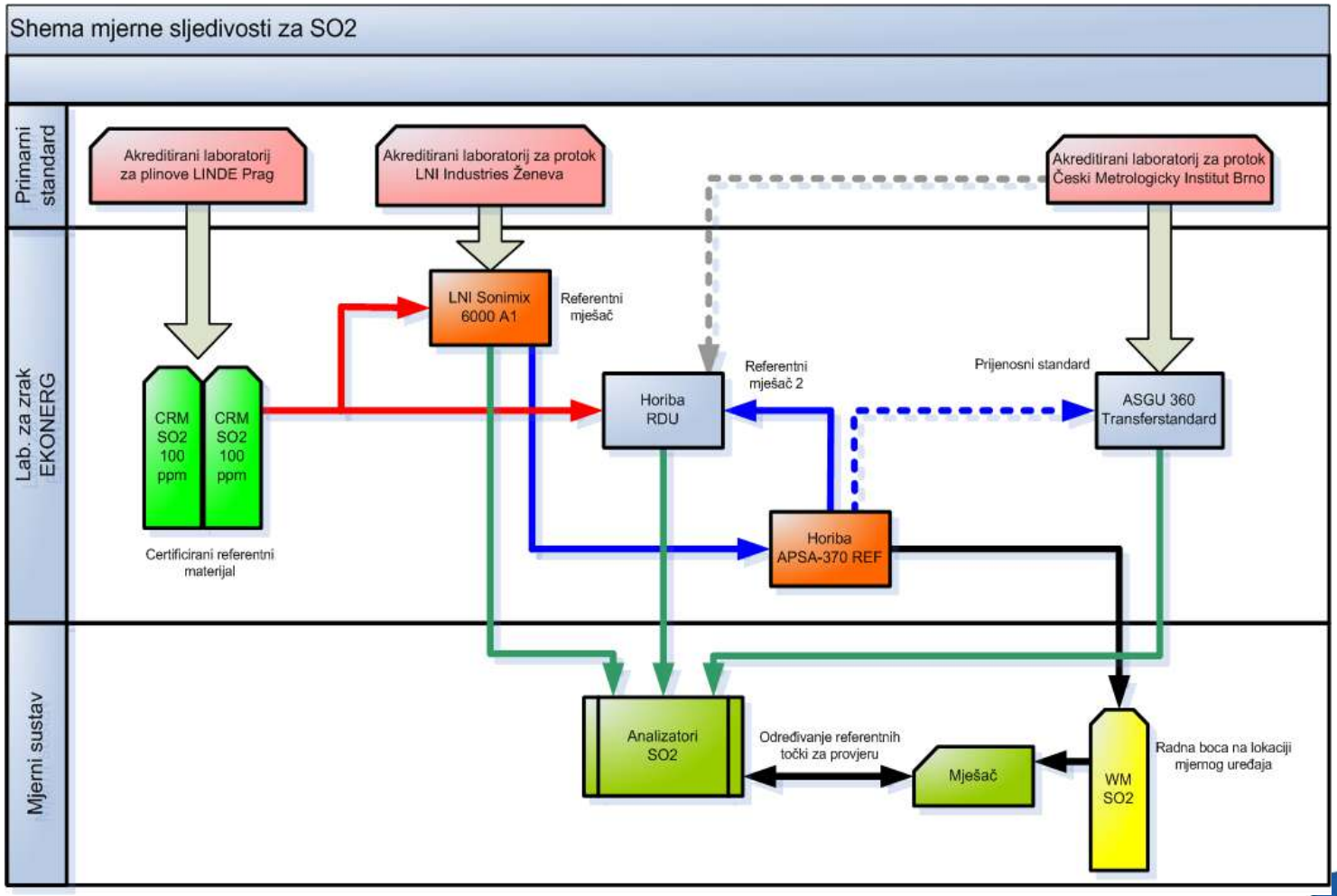

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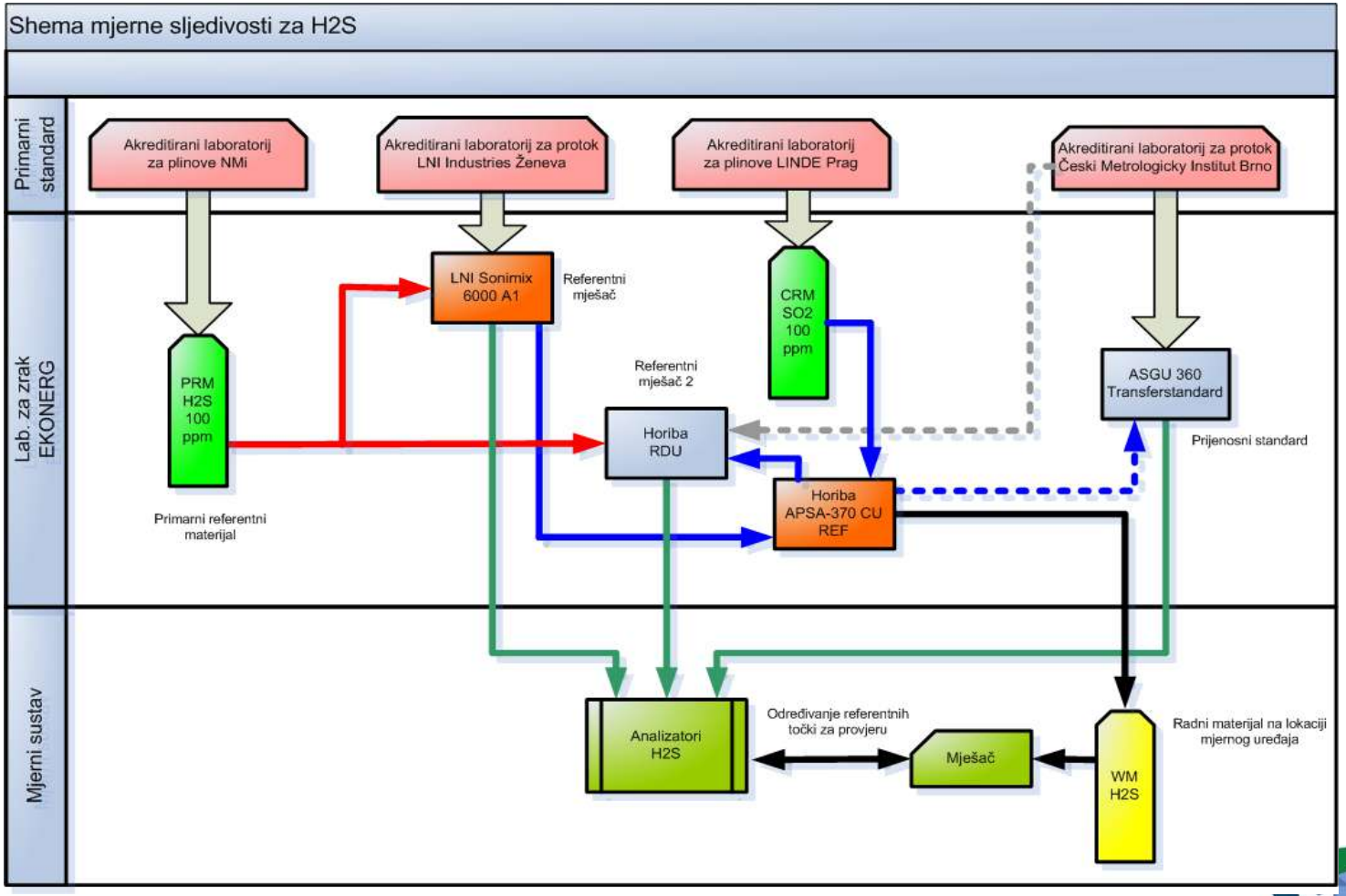

6.3 MEASUREMENT TRACEABILITY AND CALIBRATION LABORATORY

Only traceable instruments achieve valid results !!!!

6.3 MEASUREMENT TRACEABILITY AND CALIBRATION LABORATORY

6.4 Interlaboratory comparisons (Proficiency testing)

Quality assesment

Interlaboratory comparisons are an additional process for assuring and verifying accuracy and traceability (Quality assessment).

These measurements are actually measurements of the same gas in several laboratories at the same time. For the gaseous pollutants are organized in laboratory conditions.

With the help of specially designed systems, it is possible to measure the pollutants of known concentrations simultaneously.

6.4 Interlaboratory comparisons (Proficiency testing)

Interlaboratory comparisons represent the highest level in the process of harmonization of measurement and in Europe they are organized by the European Commission (through its ERLAP reference laboratory) in cooperation with the World Health Organization. Each the national reference laboratory of the European Union Member State is obliged to perform Interlaboratory comparisons with its reference instruments at least once every three years. National Reference Laboratories then organize such Interlaboratory comparisons for laboratories in their countries.

6.4 Interlaboratory comparisons (Proficiency testing)

IE ERLAP JRC, Ispra –2008

6.4 Interlaboratory comparisons (Proficiency testing)

EKONERG, Zagreb –2014

6.4 Interlaboratory comparisons (Proficiency testing)

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After the measurement is completed, the measurement results of each laboratory are compared and analysed. The results of each laboratory's measurement must meet certain criteria in terms of measurement accuracy and expressed measurement uncertainty for each measured concentration.

6.4 Interlaboratory comparisons (Proficiency testing)

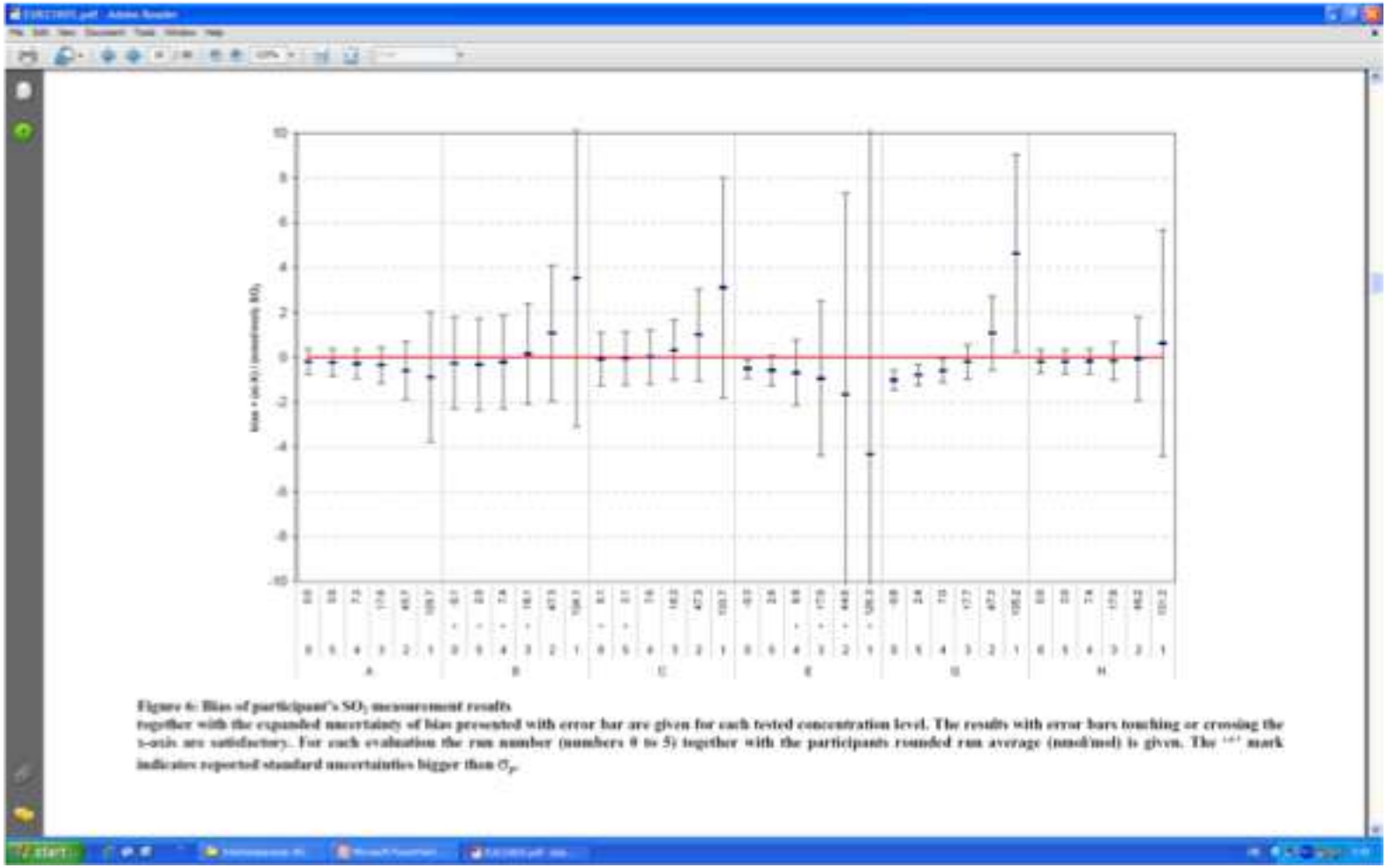

Figure 6: Bias of participant's SO_2 measurement results
together with the expanded uncertainty of bias presented with error bar are given for each tested concentration level. The results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '+' mark indicates reported standard uncertainties bigger than σ_p.

6.4. Interlaboratory comparisons (Proficiency testing)

Rezultati IS 01/2014. za CO

Lab.	Konc. (X)	Izvješteni podatci							Statistički podatci				Ocjena	
		Pojedinačne koncentracije			u_{sl}	U_{sl}	U_{sl} (%)	x_i	SDx_i	z' skor	En br.	"bias" x_i-X	Ocjena za konc.	Ukupna ocjena
A	c0 / 0	0,090			0,600	1,200		0,090		0,862	0,075	0,090	a2	zadovoljava
	c1 / 13,400	13,500	13,260	13,670	0,280	0,560	4,16%	13,477	0,206	0,096	0,063	0,047	a1	
	c2 /9,009	9,000	9,110	9,350	0,180	0,360	3,93%	9,153	0,179	0,404	0,295	0,144	a1	
	c3 /4,431	4,190	4,330	4,560	0,100	0,200	4,59%	4,360	0,187	-0,319	-0,272	-0,071	a1	
B	c0 / 0	-0,010			0,059	0,118		-0,010		-0,267	-0,257	-0,030	a1	zadovoljava
	c1 / 13,400	13,214	13,191	13,189	0,326	0,652	4,94%	13,198	0,014	0,034	0,023	0,017	a1	
	c2 /9,009	8,815	8,813	8,809	0,218	0,436	4,95%	8,812	0,003	-0,100	-0,073	-0,036	a1	
	c3 /4,431	4,295	4,303	4,299	0,118	0,236	5,49%	4,299	0,004	-0,408	-0,376	-0,091	a1	
C	c0 / 0	-0,085			0,250	0,500		-0,085		-0,814	-0,169	-0,085	a2	zadovoljava
	c1 / 13,400	13,875	13,846	13,820	0,625	1,249	9,02%	13,847	0,028	0,855	0,311	0,417	a2	
	c2 /9,009	9,139	9,131	9,127	0,412	0,824	9,02%	9,132	0,006	0,346	0,139	0,123	a2	
	c3 /4,431	4,203	4,194	4,206	0,189	0,379	9,02%	4,201	0,006	-1,032	-0,555	-0,230	a1	
D	c0 / 0	0,049			0,053	0,107		0,049		0,469	0,399	0,049	a1	zadovoljava
	c1 / 13,400	13,302	13,283	13,275	0,225	0,450	3,39%	13,287	0,014	-0,294	-0,216	-0,143	a1	
	c2 /9,009	8,868	8,875	8,846	0,166	0,332	3,75%	8,863	0,015	-0,439	-0,311	-0,146	a1	
	c3 /4,431	4,321	4,327	4,329	0,079	0,158	3,65%	4,326	0,004	-0,473	-0,456	-0,105	a1	
E	c0 / 0	-0,048			0,240	0,480		-0,048		-0,460	-0,099	-0,048	a2	zadovoljava
	c1 / 13,400	13,601	13,580	13,595	0,613	1,226	9,02%	13,595	0,006	0,339	0,125	0,165	a2	
	c2 /9,009	9,278	9,262	9,259	0,418	0,836	9,02%	9,266	0,010	0,721	0,286	0,257	a2	
	c3 /4,431	4,406	4,351	4,352	0,197	0,394	9,02%	4,370	0,031	-0,275	-0,143	-0,061	a1	
F	c0 / 0	-0,024			0,092	0,184		-0,024		-0,230	-0,124	-0,024	a1	zadovoljava
	c1 / 13,400	13,300	13,281	13,270	0,137	0,274	2,06%	13,284	0,015	-0,300	-0,262	-0,146	a1	
	c2 /9,009	8,859	8,860	8,867	0,095	0,190	2,14%	8,862	0,004	-0,412	-0,385	-0,147	a1	
	c3 /4,431	4,275	4,279	4,285	0,055	0,110	2,57%	4,280	0,005	-0,679	-0,752	-0,151	a1	
G	c0 / 0	-0,030			0,050	0,100		-0,030		-0,267	-0,257	-0,030	a1	zadovoljava
	c1 / 13,400	13,450	13,450	13,440	0,269	0,538	4,00%	13,447	0,006	0,034	0,023	0,017	a1	
	c2 /9,009	8,970	8,970	8,980	0,179	0,358	3,99%	8,973	0,006	-0,100	-0,073	-0,036	a1	
	c3 /4,431	4,340	4,340	4,340	0,087	0,174	4,01%	4,340	0,000	-0,408	-0,376	-0,091	a1	

6.3 Interlaboratory comparisons (Proficiency testing)

Quality assesment

- **ACCREDITATION HRN EN ISO/IEC 17025**
  - **Internal independent audit 1 per year**
  - **HAA audit 1 per year**
  - **Reaccrediation every 5 years**

EKONERG Energy Research and Environmental Protection Institute

INZRAK

THANK YOU FOR YOUR ATTENTION

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