Metrology for Chemical Pollutants in Air

Preparation of VOC transfer standards for indoor air applications

ENV01 JRP MACPoll D3.3.2

Presentation at BAM
February 13, 2014

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Dita Heikens (VSL)
Marivon Corbel (NPL)

National Physical Laboratory

VSL

Outline

Part 1 by Dita Heikens (VSL)

- **Introduction**
- **VSL research activities within MACPoll**

Part 2 by Marivon Corbel (NPL)

- **NPL research activities within MACPoll**
- **Results of cross-check study**

Introduction

Aim of research

- Increasing health problems due to indoor material emissions.
- To give traceability for the measurement of (S)VOC in indoor air and constant emitting materials
- Develop suitable sampling techniques, measurement methods and preparation methods for (S)VOC

Selection of components

- Selection of at least three priority (S)VOC compounds that are indoor pollutants and need measurement traceability.

Cross-check study

- To check the comparability of the developed measurement approaches and to check the preparation of reference materials

Selected components

Component with CAS number	Molecular formula	Molar mass (g/mol)	BP at 101 kPa (°C)	Vapour pressure at 20 °C (kPa)
Styrene 100-42-5	C_8H_8	104.150	145	0.62E-01
1-Methyl-2-pyrrolidone (NMP) 872-50-4	C_5H_9NO	99.131	202	3.47E-02
2-Ethyl-1-hexanol 104-76-7	$C_8H_{18}O$	130.228	184	2.00E-02
Dimethyl phthalate (DMP) 131-11-3	$C_{10}H_{10}O_4$	194.180	282	2.82E-04
Hexadecane 544-76-3	$C_{16}H_{34}$	226.440	287	1.09E-04
Dibutyl phthalate (DBP) 84-74-2	$C_{16}H_{22}O_4$	278.340	340	9.07E-07

Cross-check study

Performed by BAM, NPL and VSL

VSL has generated standard atmospheres of the (S)VOC (reference gas mixtures)

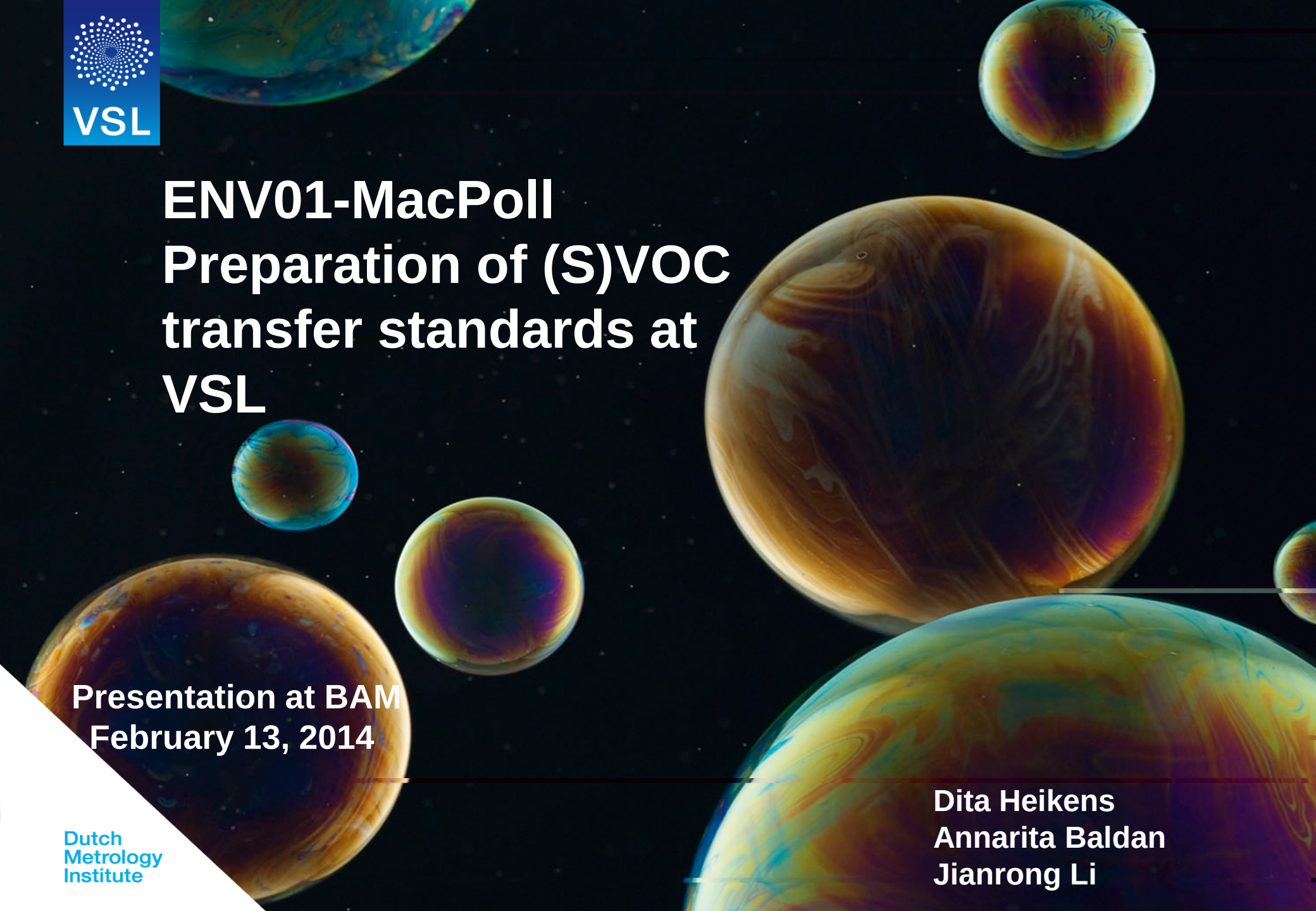
- **Loading tubes: target values 30 and 100 ng**

and subsequently

BAM has prepared liquid reference standards

- **Spiking tubes: target values 30 and 100 ng**

Analysis of the tubes by BAM, NPL and VSL



ENV01-MacPoll Preparation of (S)VOC transfer standards at VSL

Presentation at BAM
February 13, 2014

Dita Heikens
Annarita Baldan
Jianrong Li

Dutch Metrology Institute

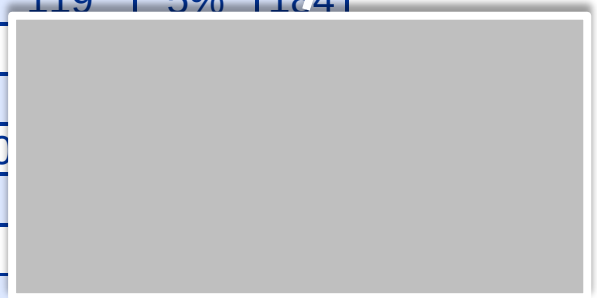
Contents

- Generation system of (S)VOC gas mixtures
- Preparation of transfer standards
- Analytical method
- Validation of VSL's (S)VOC generation system and transfer standards
- Results of validation
- Conclusion

Dutch
Metrology
Institute

Gas generation system (ISO 6145-4) with 1 stage dilution

Possibilities Components	Concentration Min ($\mu g/m^3$)	 Max ($\mu g/m^3$)	U (k=2)	BP (°C)
hexane (n-C6)	30	>500	3%	69
toluene	30	>500	3%	111
1-octene	100		3%	123
styrene	30	>500	3%	145
n-decane (n-C10)	30	>500	3%	174
2-ethyl-1-hexanol	30	119	5%	184
1-methyl-2-pyrrolidone (NMP)	30			
benzylalcohol	30			
1-dodecene	100			
dodecamethylcyclohexasiloxane	30			
butylated hydroxytoluene (BHT)	30			
dimethyl phthalate (DMP)	30	120	5%	282
hexadecane (n-C16)	30	400	5%	287
diethyl pthalate (DEP)	30	400	5%	296
n-octadecane (n-C18)	30	320	5%	317
dibutyl phthalate (DBP)	30	67	10%	340
eicosane (n-C20)	30	60	~10%	343



Continuous injection

Dutch Metrology Institute

Gas generation system (ISO 6145-4) new development with 2 stage dilution

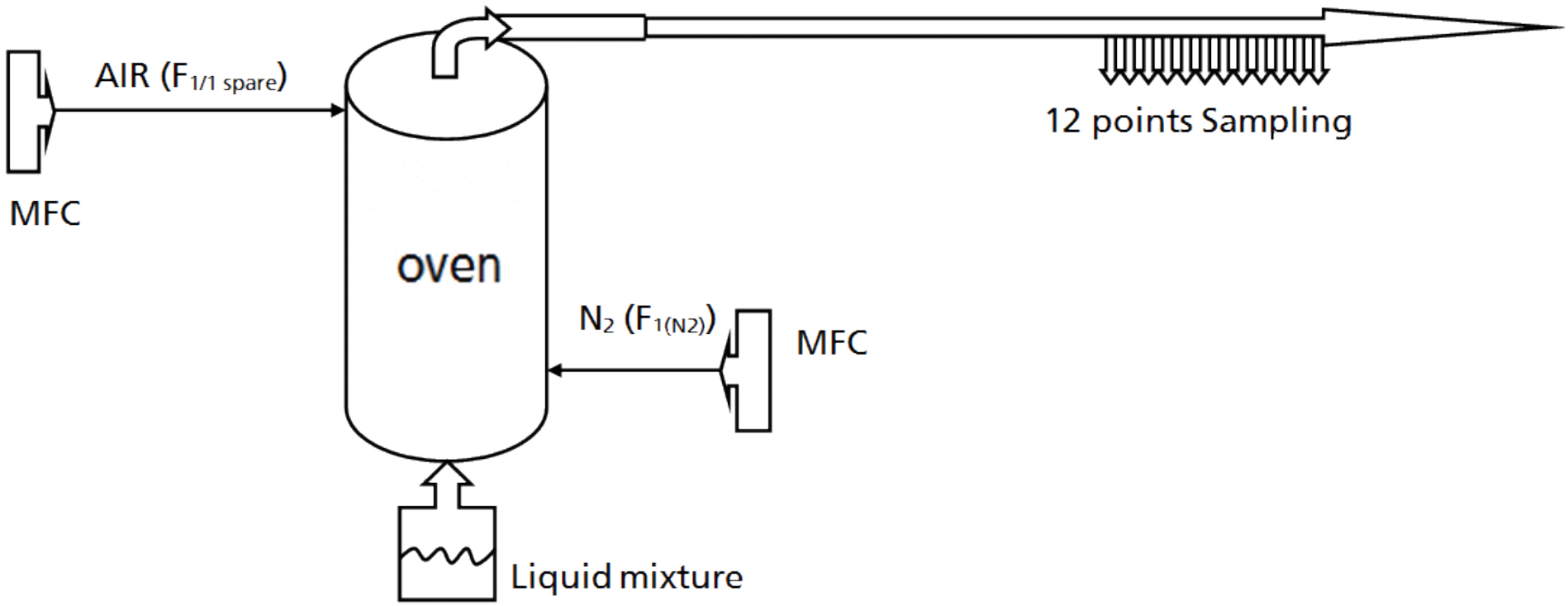
Goal:
Generation of concentrations at (sub) ppb level
(10 µg/m^3- 1 µg/m^3)

First tests done with:
n-Hexane 425 µg/m^3
n-Hexadecane 100 µg/m^3

Continuous injection

Dutch Metrology Institute

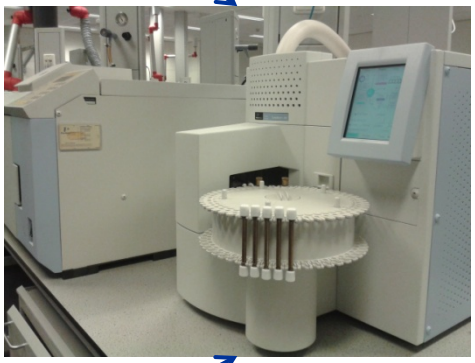
Schematic drawing dilution system

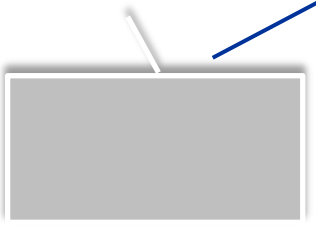


Traceable to mass and volume

Dutch
Metrology
Institute

Preparation and validation of (S)VOC transfer standard





Dutch Metrology Institute

Example of preparation of an (S)VOC loaded standard

Preparation of loaded standard tubes with gas generation system (ISO 6145-4)		
Sample concentration	~69 ng/L ~10 ppb	
Tube	TD tube-type	
Sorbent material	Tenax TA®	
Pumping flow	50 mL/min	
Sampling volume	1.5 L	0.45 L
loading level	100 ng	30 ng
Flushing all tubes with 0.5 L purified air		

Dutch Metrology Institute

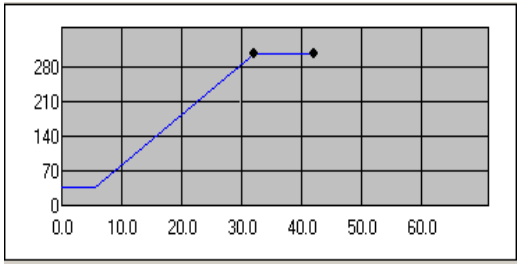
Validation

Preparation of liquid spiked tubes for validation		
Spiking concentration	6.1 µg/g	1.64 µg/g
Spiking volume	20 µL	20 µL
spiking level	100 ng	30 ng
Flushing all tubes with 1.0 L purified air		

Analytical Method ATD-GC-FID

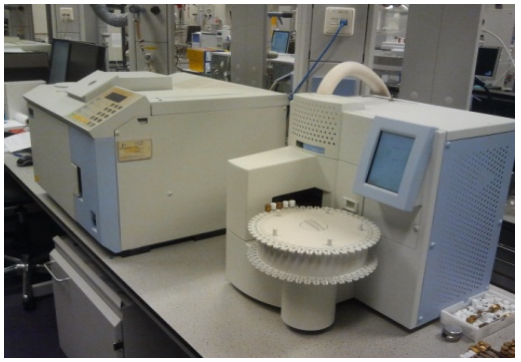
ATD settings		
First desorption	Time (min)	5
	Tube temperature(°C)	300
	Trap temperature (°C)	-30
	Desorption flow (mL/min)	30
	Inlet split (mL/min)	0
Second desorption	Time (min)	3
	Trap temperature (°C)	300
	Temperature gradient (°C/s)	99
	Outlet split (mL/min)	7
	Carrier gas	Helium
	Valve temperature (°C)	300
	Line temperature (°C)	300
	Trap	Tenax TA

GC-FID settings		
Column/trap flow		1.5 mL/min
Column		CPSil8 CB 60m x 0.32mm x 0.25 µm
FID	temperature	350 [ºC]
	H2 flow	45 mL/min
	Air flow	450 mL/min



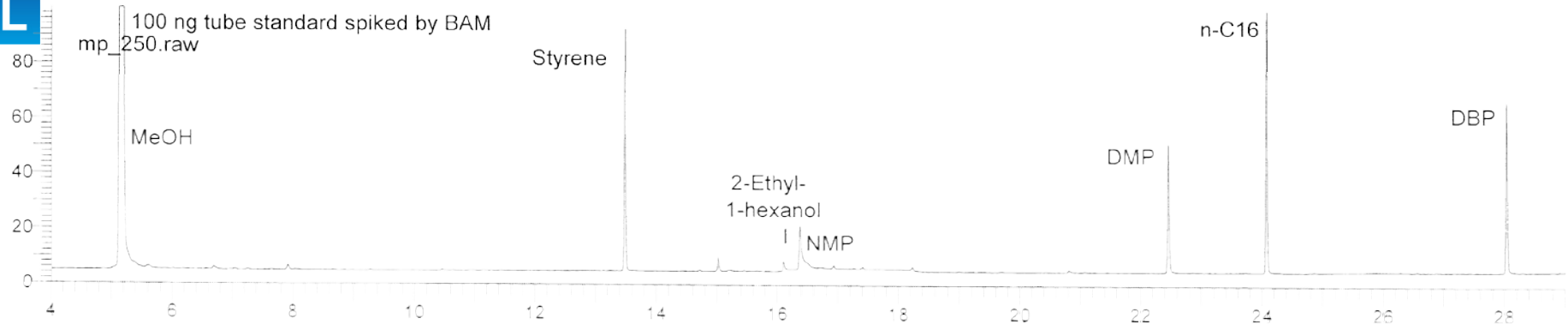
Oven Ramp	Rate	Temp	Hold
Initial	0.0	40	5.50
1	10.0	300	10.00
2	0.0	0	0.00
3	0.0	0	0.00

Oven Ramp



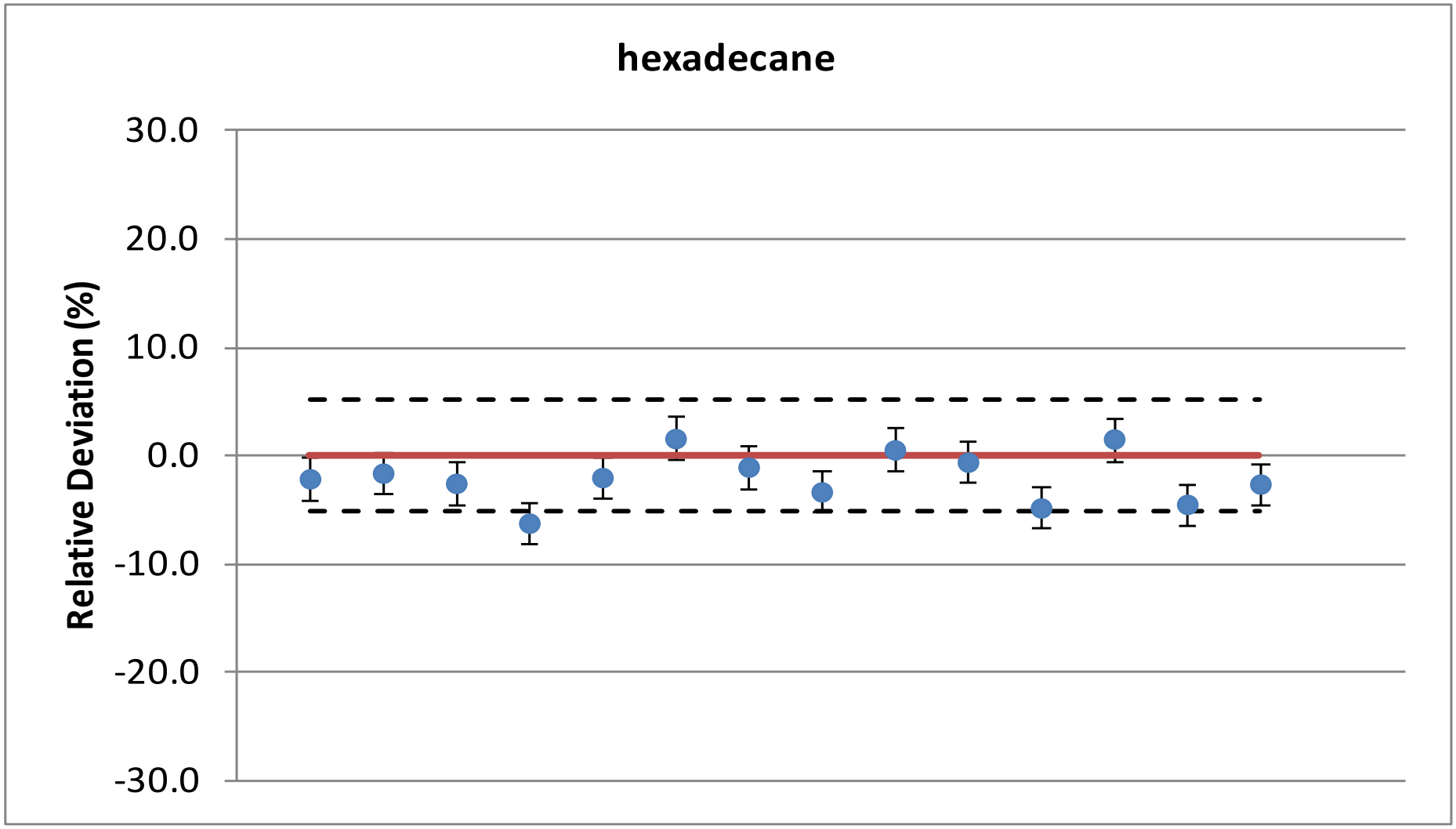
Dutch Metrology Institute

Example of GC-FID chromatogram



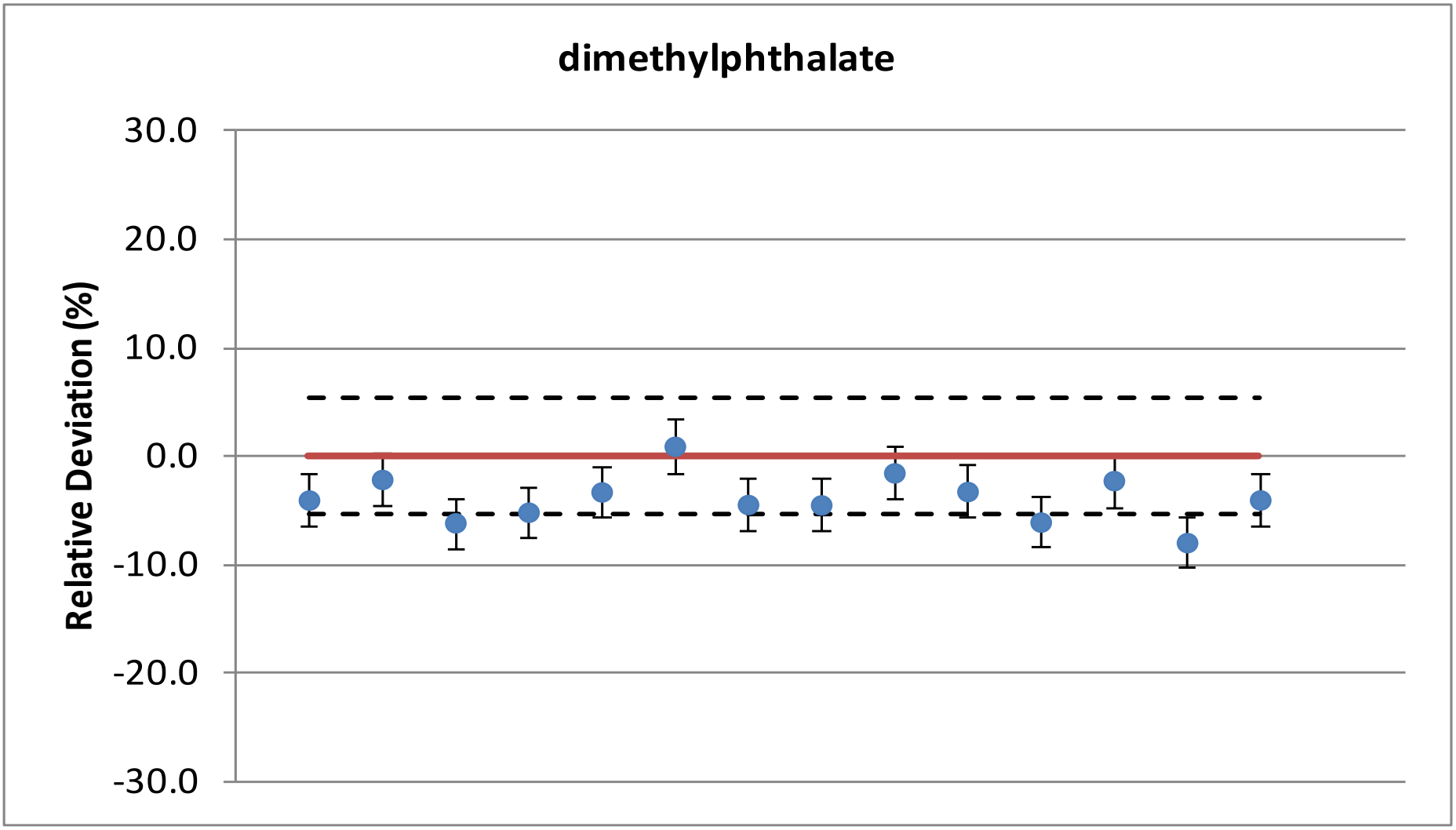
Dutch Metrology Institute

Results of validation



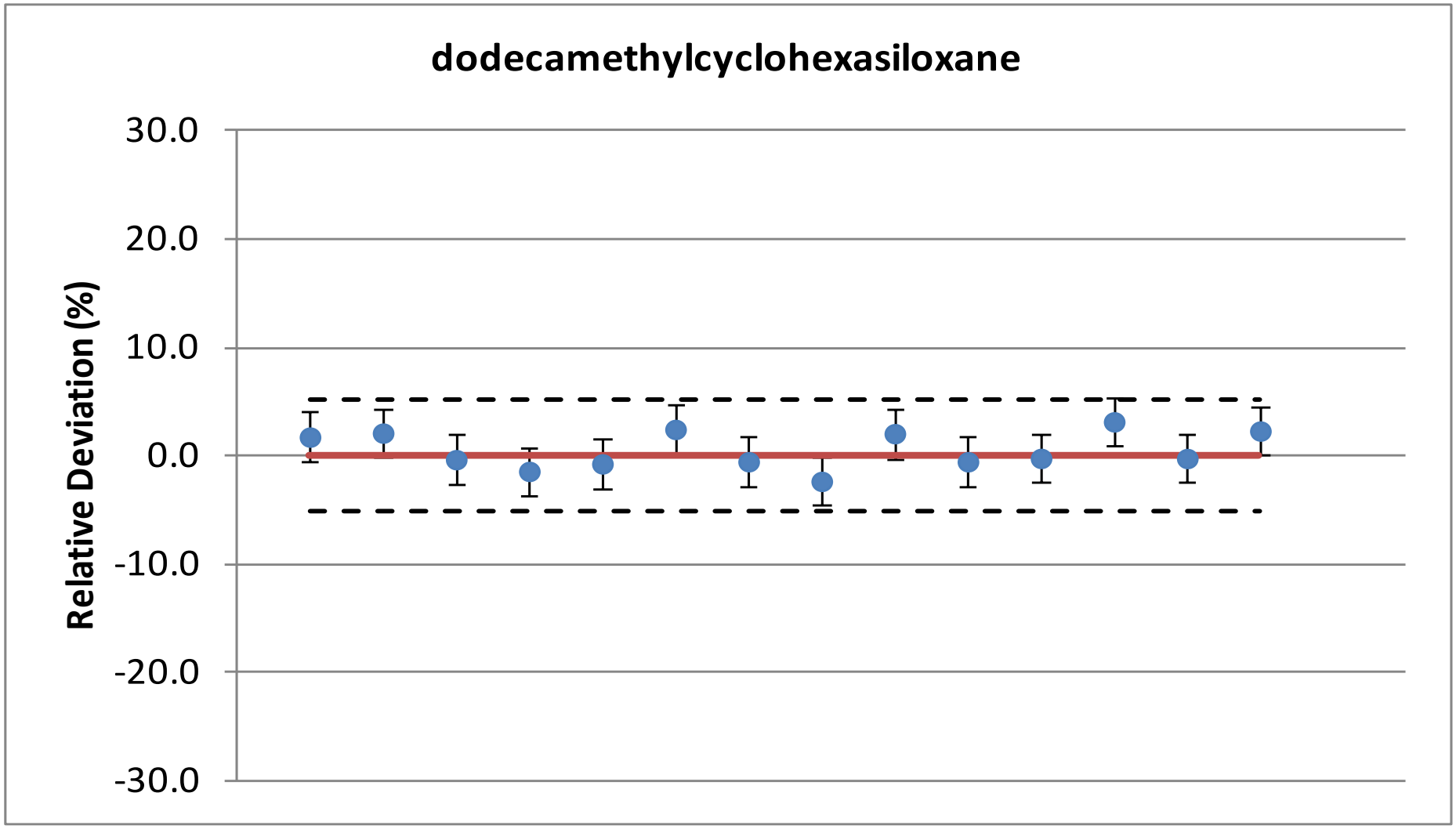
Dutch
Metrology
Institute

Results of validation



Dutch
Metrology
Institute

Results of validation



Dutch
Metrology
Institute

Conclusions

- VSL's generation system is validated for the generation of standard atmospheres of (S)VOC gasmixtures
- The preparation uncertainty for most (S)VOC components is ≤ 5% (k=2)
- The preparation uncertainty for DBP and n-C20 is ≤ 10% (k=2)

- The long term stability of the (S)-VOC transfer standard is under investigation

Dutch Metrology Institute

Contact information

Annarita Baldan (Project coordinator)

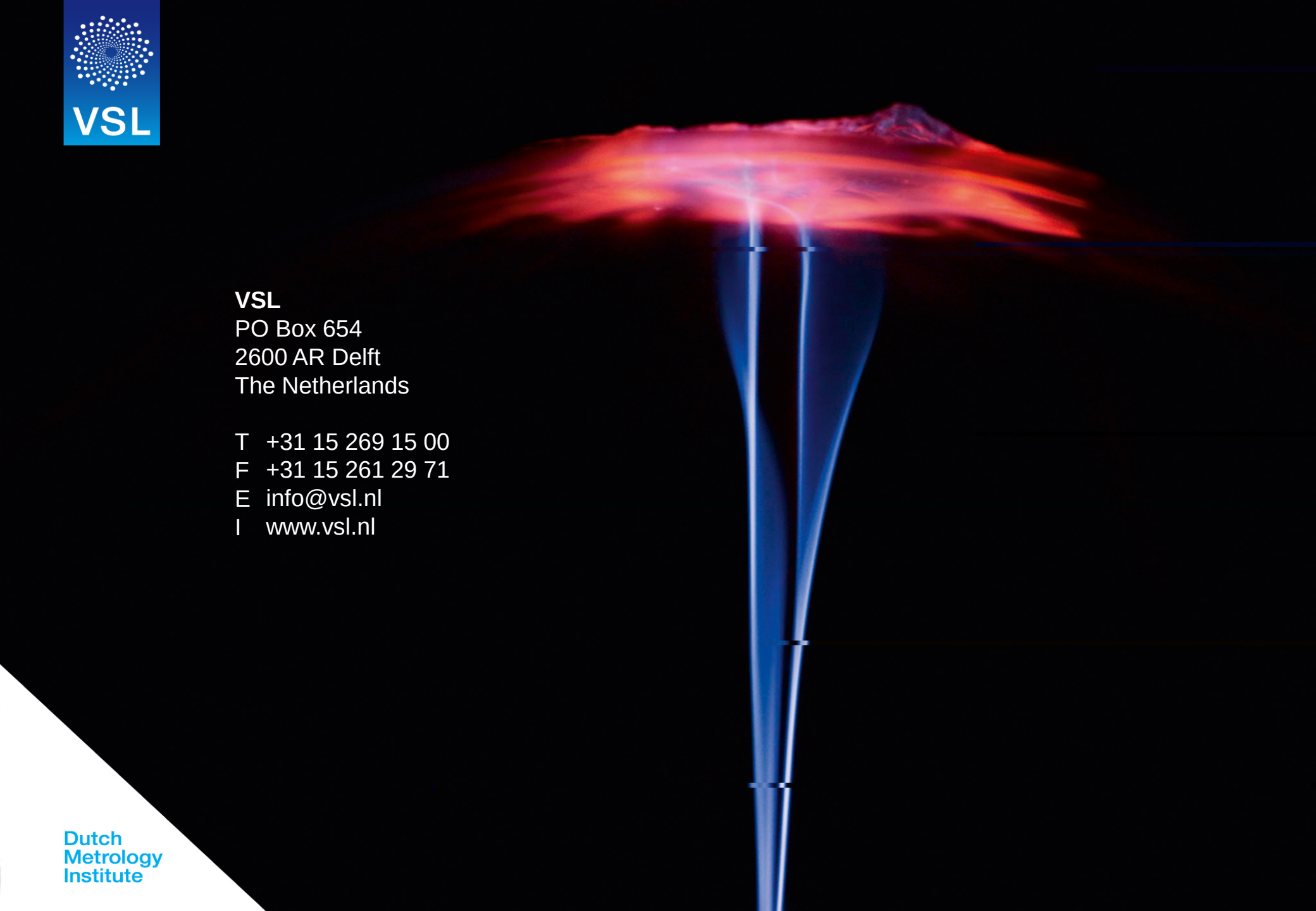
Jianrong Li (Data processing)

Dita Heikens (preparation, analysis and data processing)

Contact

ABaldan@VSL.nl or info@VSL.nl

Dutch Metrology Institute



VSL
PO Box 654
2600 AR Delft
The Netherlands

T +31 15 269 15 00
F +31 15 261 29 71
E info@vsl.nl
I www.vsl.nl

Dutch
Metrology
Institute