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Highlights of Analytical Chemistry in Switzerland

Calibrating Sensitive Analytical Instruments – or How Much is 'Zero'?

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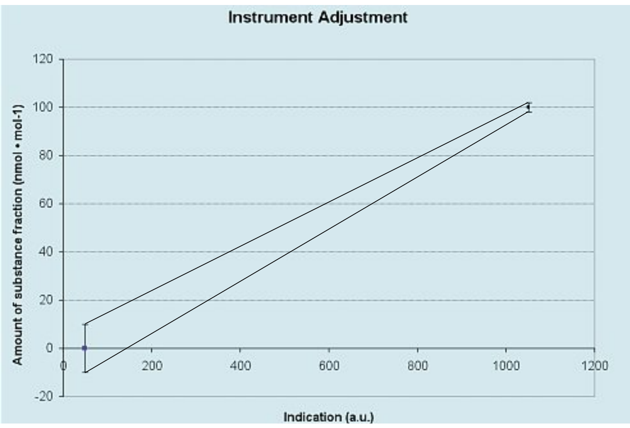
Monitoring the ground-level air quality requires sensitive gas analysers capable of detecting air pollutants at the nmol • mol^{-1} or mm^3 • m^{-3} level. Quality systems require *e.g.* that gas analysers be periodically adjusted with certified reference gas mixtures for the span points and with so-called zero gas for the zero point. At low concentration values however already trace amounts of analytes in the zero gas at the time of instrument adjustment contribute considerably to the measurement uncertainty.

Under field conditions it is not guaranteed that zero air generators are working permanently as specified, specially *e.g.* at periods of high ambient air pollutant concentrations or extreme weather conditions. Residual amounts of analytes may therefore accidentally be present in zero air and cause adjustment and thus measurement errors.

METAS has therefore established the infrastructure to measure traces of numerous pollutants in zero air from zero air generators under simulated operating conditions allowing specifying residual amounts of analytes under close application conditions.

To measure the performance of zero air generators, they are fed with a series of standard gas mixtures with known 'worst case' ground-level concentrations. Ambient air concentrations vary with time and can not be used for this purpose. For the detection of the remaining analyte traces the best suited, *i.e.* most sensitive and specific available analytical methods are used. For *e.g.* NO and NO_2 it is the chemiluminescence method with O_3, for CO non-dispersive infrared absorption. The sample with the unknown amount is the outlet gas mixture of the generator.



The trend of the measurement uncertainty contribution for the instrument adjustment at the zero point with an assumed uncertainty of 10 % and at the span point at 100 (nmol • mol^{-1}) of 2 % for the standard gas mixture, respectively, is shown.

Summary of test results for three analytes for a modern zero air generator, the specifications and regulatory requirements. *U:* expanded uncertainty with a confidence interval of ≈ 95 % for values above the detection limit. [a]Detection limit. [b]Sum of x NO_2 and x *NO*. n.s.: not specified.

Sample	Amount of substance fraction (x) of analyte (nmol • mol^{-1})					
	x NO_2	U	x NO	U	x CO	U
Standard gas mixture at inlet	76.7	1.0	65.0	0.8	2025	22
Outlet gas	<0.7[a]		0.7	0.2	<6[a]	
Specifications of generator	<1[b]		<1[b]		<10	
Swiss regulatory requirements for zero air	<0.56		n.s.		urban: <88.5 rural: <8.8	

The results show, that this zero air generator meets the specifications and regulatory requirements under the test conditions. The chemiluminescence method for NO_2 and NO is just fit for purpose to reach the necessary detection limits.

Measurement capabilities are presented for testing the performance of zero air generators under close operating conditions. The analytical methods meet the required sensitivities for critical analytes, but need further developments for other analytes, *e.g.* CH_4, to approach 'zero' closer

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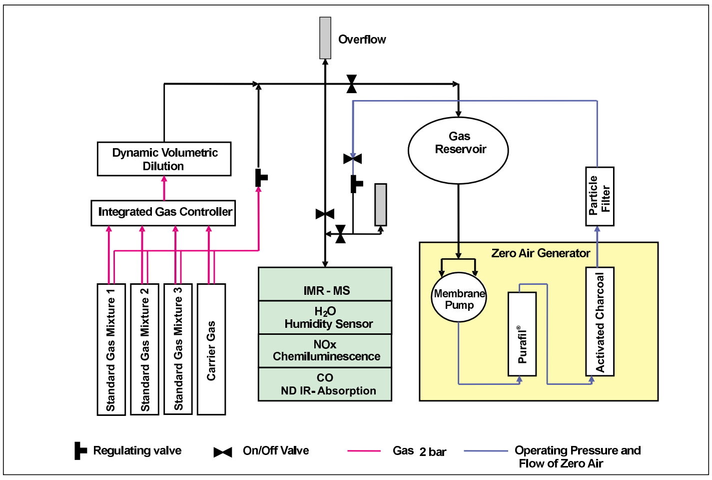

Schematic of measurement set-up for zero air generators with the gas supply and the analytical methods. IMR-MS: ion molecule reaction mass spectrometer. The zero air generator is shown only with the compressor and the final filter elements.

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