
Mercury in the Workplace: air monitoring and exposure assessment procedures

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Talk Summary



- **Workplace Exposure Assessment**
 - Workplace air monitoring
 - Biological monitoring
- **Speciation in Air Monitoring and Emerging Instrumentation**
 - Stack (point) air monitoring
 - Ambient air monitoring
 - Natural gas/landfill gas/fugitive emissions

Workplace Exposure Assessment



- **Workplace activities where exposure to mercury can occur**
 - Chloroalkali industry
 - Instrument manufacture and repair
 - Battery/lamps/electrical switches manufacturing
 - Dentistry and (chemical) laboratories
- **Emerging and reoccurring workplace activities**
 - Brown field site reclamation
 - Dismantling of old industrial plants and machinery

Workplace air monitoring

- **Workplace air limit values – Hg(0) and inorganic compounds**
- UK (HSE) EH40 WEL limit (2004)
 - 0.025 mg/m³ (25000 ng/m³ v < 10 ng/m³)
- US (ACGIH)
 - 0.025 mg/m³
- Other countries
 - 0.025 – 0.1 mg/m³
- **Workplace air limit values – organic Hg species**
 - Alkyl Hg – 0.01 mg/m³
 - Aryl Hg – 0.1 mg/m³

Workplace air monitoring



- **Personal monitoring**
 - **Pumped sampling**
 - **Diffusive sampling**
- Area (background) monitoring
 - Hand held instrumentation
 - Automatic area monitoring systems

Workplace Air Monitoring



- **Pumped sampling**
 - **SKC Anasorb tubes (Hydrar/Hopcalite)**
 - Gold trapping tubes
 - Iodine impregnated charcoal tubes
 - Pd treated or CuI impregnated filters
 - KMnO₄ impinger sampling
- **Diffusive sampling**
 - **SKC Anasorb badges (Hydrar/Hopcalite)**
 - Gold film badges

Workplace air monitoring

- SKC Anasorb tubes and badges



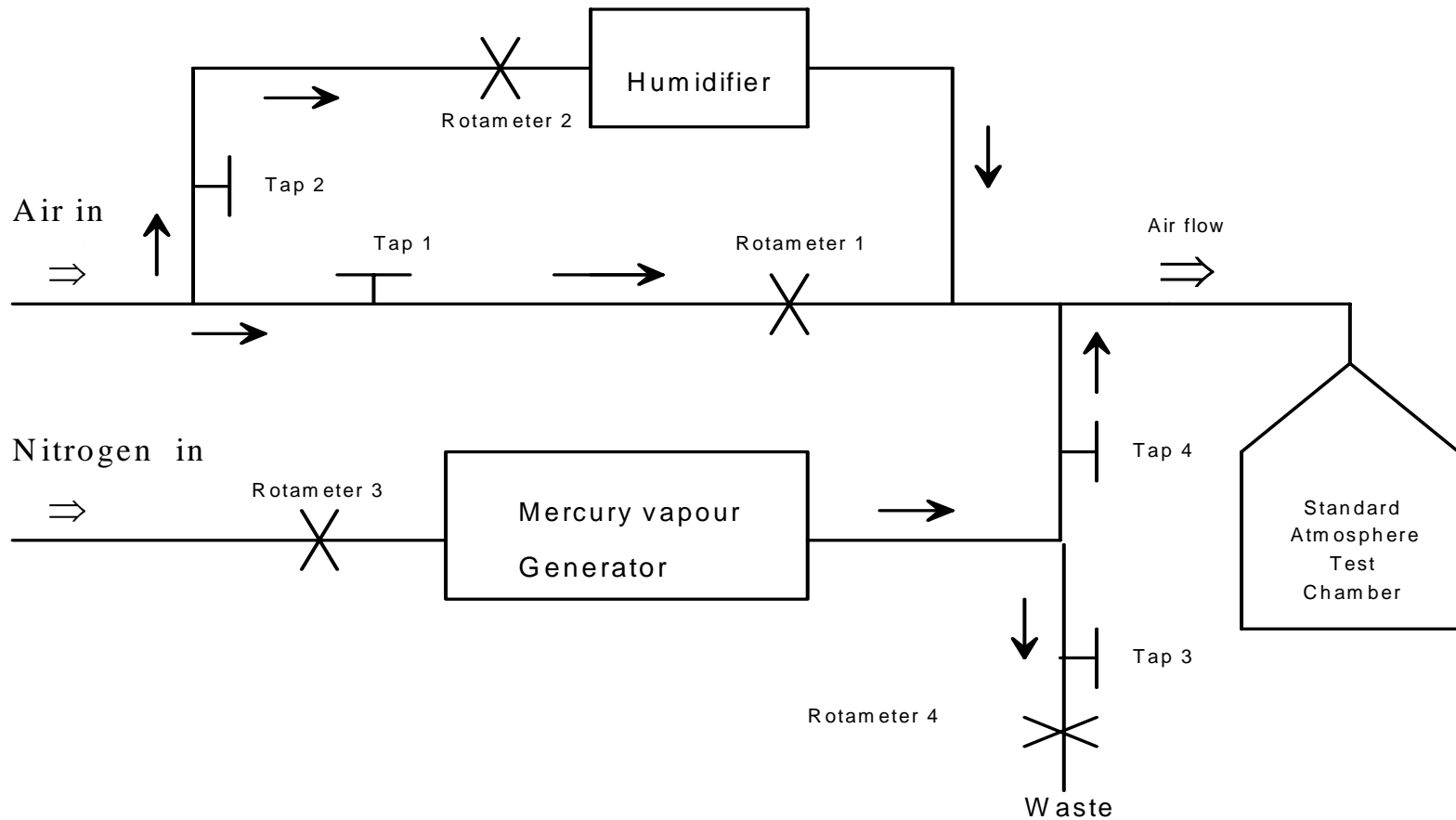
Workplace Air Monitoring

- **SKC Anasorb tubes/badges (Hydrar/Hopcalite)**
 - Cu/Mn oxide based sorbent on alumina support
 - Tubes – 200 mg and 500 mg sorbent tubes
 - Badges – 800 mg sorbent tubes
- **Sample Preparation**
 - Digests easily in nitric/hydrochloric acid mixture

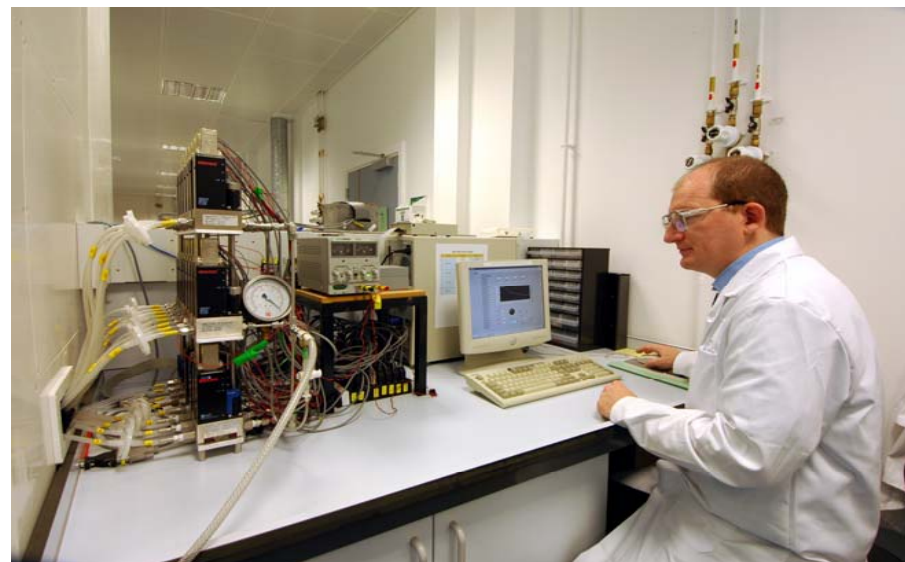
Workplace Air Monitoring

ng Hg /sampling tube	FI-CVAAS (PE 5100 AAS)	CVAFS (PSA Merlin)	Discrete CVAAS (Cetac M6100)	TCAAS (Milestone DMA-80)	ICP-MS (PE Elan 6100)
LoD	9	2	1	2 ?	15
LoQ	30	8	3	8 ?	50
Comments	Cold vapour Modified AAS	Cold vapour 1995 Model (derated)	Cold vapour New instrument (derated)	Instrument LoQ < 0.5 Upper range?	Solution analysis Sample introduction Memory effects


Dynamic gas generation systems

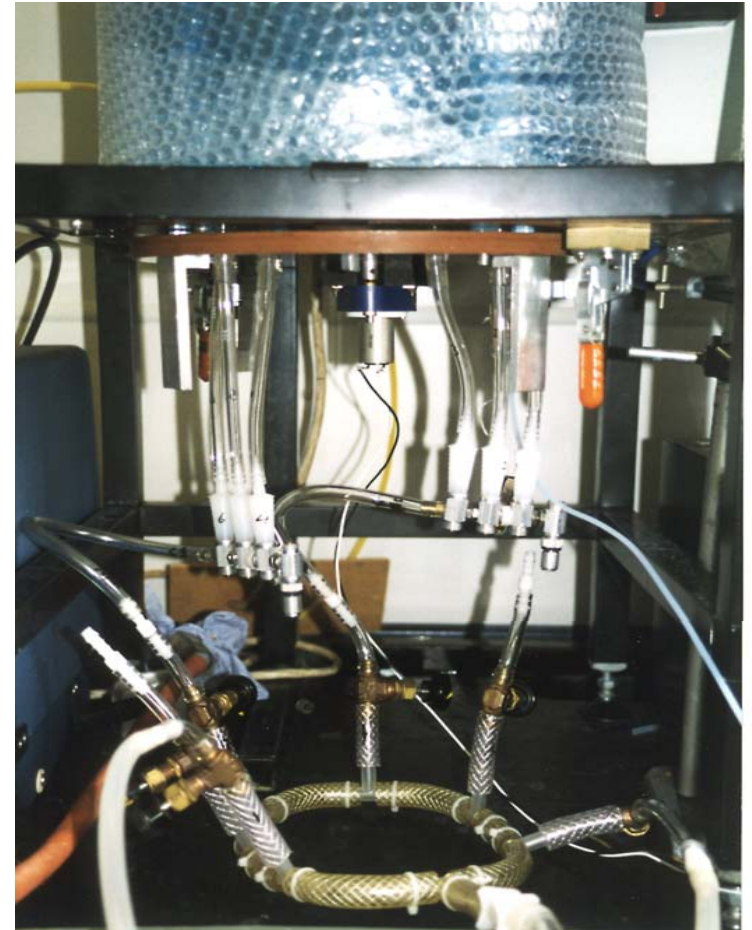
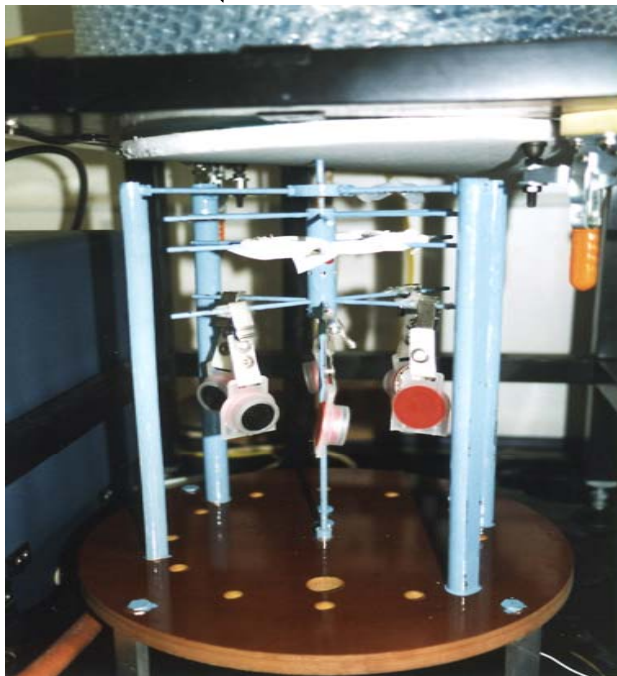


Dynamic gas generation systems



Dynamic gas generation systems

- Pumped
 - Passive
- sampling
validation
- 



Workplace Exposure Assessment



- **Status of Standardised methods**
 - ISO 17733 (hydrar sampling tubes:CVAAS/AFS)
 - ISO 20552 (Au sampling tubes:CVAFS) - 2007
- **Related standards**
 - EN 482: Performance of methods for workplace measurements
 - EN 838 and 1076: Performance tests for diffusive samplers

Workplace Air Monitoring

Active v diffusive paired test	Number of pairs	Slope	Correlation (R2)
Chloroalkali plant	17	0.56	0.97
Thermometer factory	18	0.76	0.88
Dentistry	18	0.48	0.91

Biological Monitoring

- **Urine/blood monitoring**
- UK (HSE) Health Guidance Value
 - 20 $\mu\text{mol Hg/mol creatinine}$ (urine)
- German (DFG) BAT Value
 - 50 $\mu\text{mol Hg/mol creatinine}$ (urine)
 - 125 nmol/l (blood)
- USA (ACGIH) BEI Value
 - 20 $\mu\text{mol Hg/mol creatinine}$ (urine)
 - 75 nmol/l (blood)

Biological Monitoring

Industry sector	Mean (range) Years of exposure	Mean (range) Hg (U) $\mu\text{mol/mol}$ creatinine
Chloralkali	9.8 (0.2 – 36)	20 (4 – 75)
Battery manufacture	5.2 (0.1 – 27)	10 (1 – 126)
Instrument repair	8.4 (0.1 – 47)	9 (1 – 164)
Electrical lighting	9.6 (0.1 – 37)	5 (1 – 931)
All	7.6 (0.1 – 47)	8 (1 – 931)
Unexposed UK benchmark		< 2

Biological Monitoring

	CV total creatinine corrected (%)	CV total uncorrected (%)
Within day (n = 17)	22.4 ± 7.9	47.3 ± 22.2
Between day (n = 10)	15.6 ± 7.2	37.3 ± 23.6
Total imprecision for two consecutive spot urine samples	~ 40 – 50 % but not implying any change in body burden!	

Biological Monitoring

Analytical (combined) Precision (Creat + Hg(U))	Lower limit (mean – 2sd) nmol/mol creatinine	Upper limit (mean + 2sd) nmol/mol creatinine
4	13.9	26.1
5.5	13.8	26.2
8	13.4	26.6
10	12.9	27.1
12	12.4	27.6

Biological Monitoring - speciation



- **Biological Monitoring realities**
- Price sensitive market
- Results often required in less than 5 days and often offered 24 hour service
- **Speciation protocols**
 - Dedicated hyphenated techniques e.g. HPLC-ICP-MS not viable (today) for every day bio monitoring market for cost and throughput reasons
 - Alternatives: selective oxidation options
 - Persulphate oxidation for total Hg
 - Permanganate oxidation for inorganic Hg
 - Organic Hg by difference

Biological Monitoring

- **Hair/Nail monitoring**
 - Exogenous exposure (contamination?)
 - May reflect both occupational exposure and dietary uptake
 - May be hard to set suitable baseline (unexposed) reference value or ranges due to:
 - Historical data sets may be compromised by inadequate analytical techniques
 - Cohort (control) size insufficient and/or not clearly defined with 'unknown' exposure sources
 - But can have use for time profiling/poisoning studies

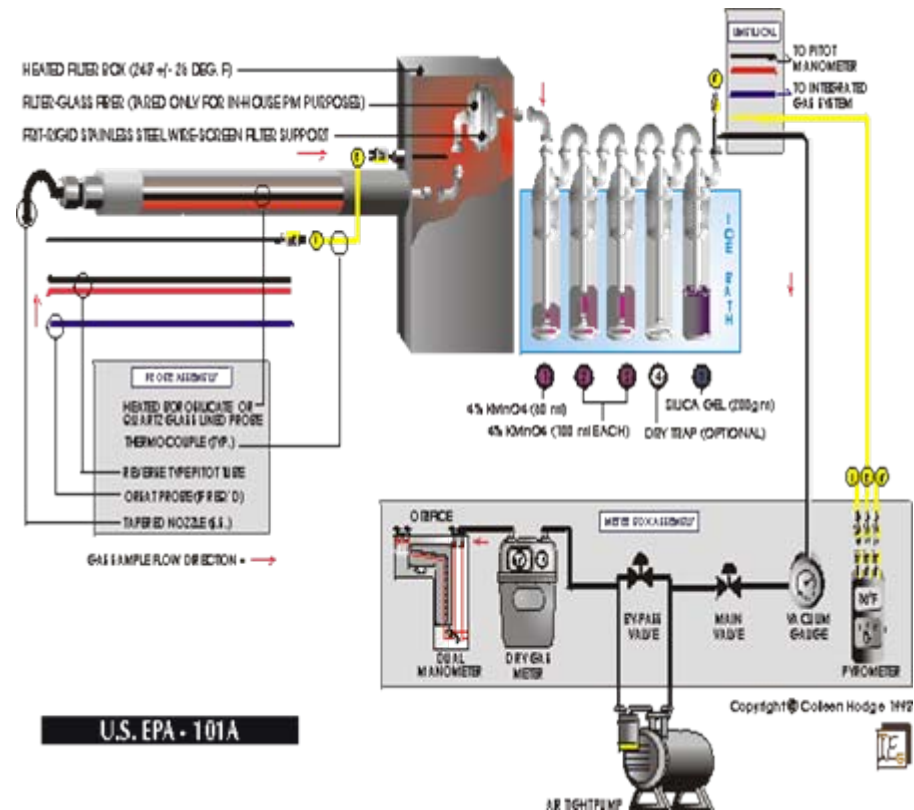
Biological Monitoring



- **Breath sampling**
 - Interest in (non occupationally exposed) body burden arising from dental amalgams
 - Intra-breath cross contamination issues with manual gold trap grab sampling
 - Interesting paper describing automated instrumented with autoflush options
 - **Halbech and Welzl Toxicology 2004 14(5) 293-299**

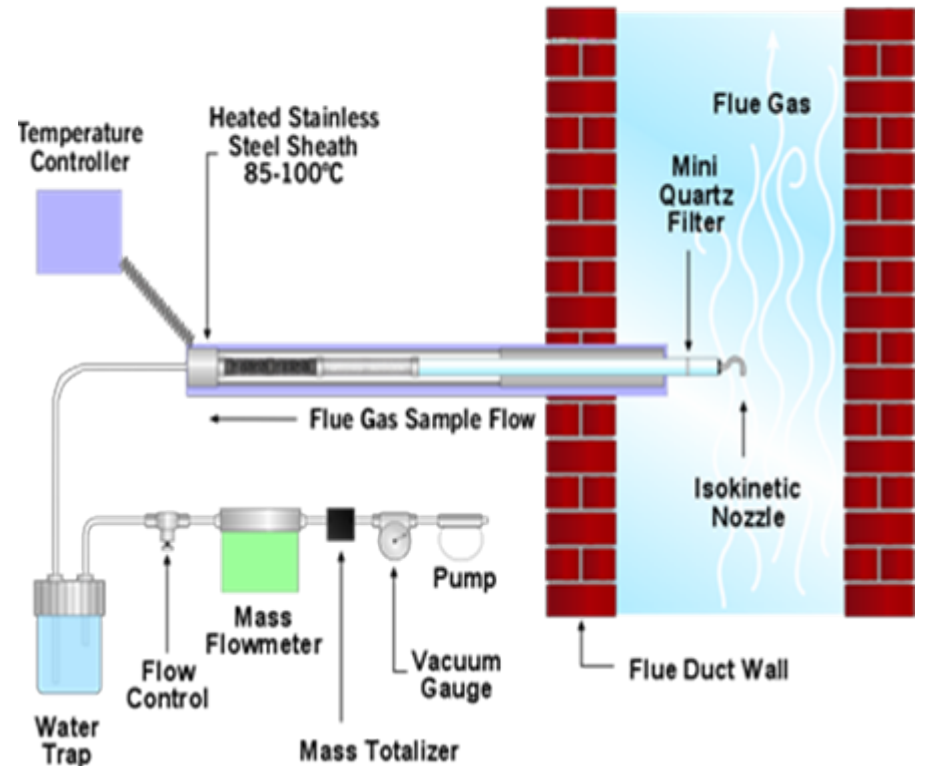
Manual Stack Monitoring Procedures

- Manual impinger systems
- Total Hg (EPA 101a)
- Speciation of Hg(0), HgX and Hg(P) (Ontario Hydro method/ASTM D6784-02)
- Laboratory analysis based upon EPA method 1631



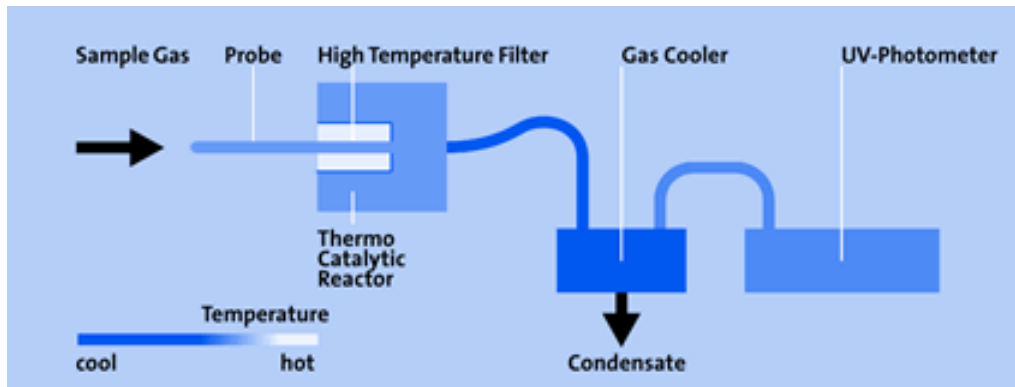
Manual Stack Monitoring Procedures

- Manual sorbent systems
- Total Hg (EPA 324)
- Speciation of Hg(0), HgX and Hg(P) (FAMS)
- Wet chemistry or Thermal combustion



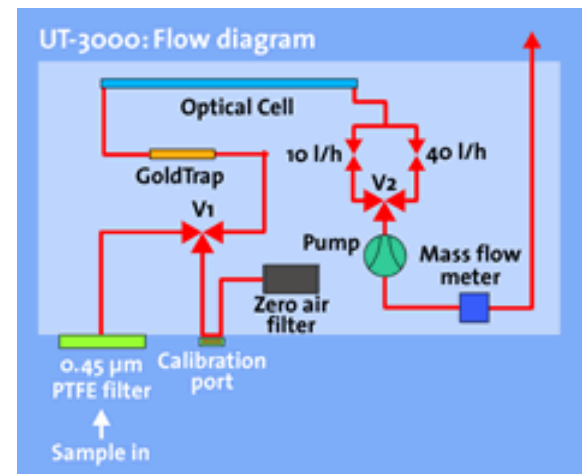
CEM Instrumentation

- New instruments for stack monitoring
- Speciation of Hg(0), HgX and Hg(P)



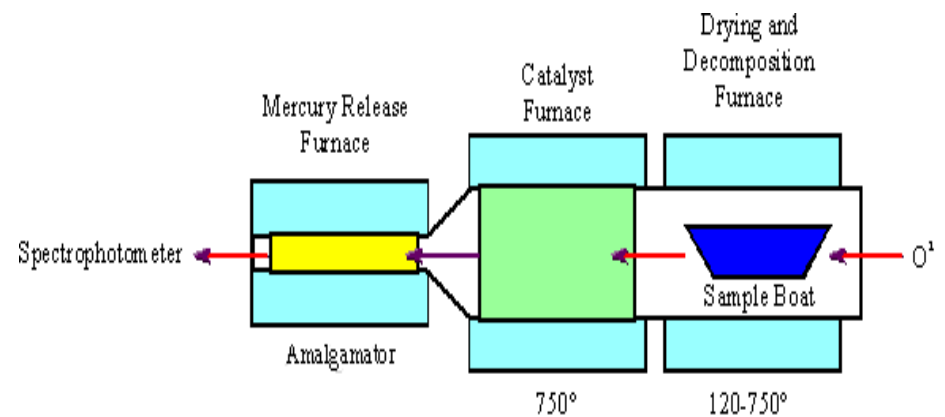
Emerging Portable Instrumentation

- New instruments for air analysis (TGM)



Emerging Portable Instrumentation

- Combustion based analysers for solid and liquid analysis



Emerging Portable Instrumentation



DMA-80 TEST	Measured mg/kg	Certified mg/kg	% mean recovery
Canmet SO-1 soil	0.090 ± 0.003	0.082 ± 0.009	110
GBW 07604 Popular leaves	0.027 ± 0.001	0.026 ± 0.006	104
FAPAS milk powder (PT)	0.034 ± 0.002	0.038 ± 0.017	90
Comments	40 place autosampler; 5 minute analysis Method LoQ = < 0.5 ng % carryover < 0.15 % (based upon 500 ng sample)		

Acknowledgements



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