METHOD VALIDATION BY EPA M301

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Method Validation

Many bodies requiring method validation

- ISO/IEC 17025

- ASTM Interlaboratory E1488

- EPA OAQPS FRM Equivalence

- EPA SW-846 Test Method Equivalence

(and even ...)

- FDA Method Validation Guidance

Method Validation Approaches

Although many differences, in general most validations depend on either

- Comparison to a known method, or

- Precision and bias of a proposed method, or

- Both

Scope of M313 Validation

Method is requested to be approved
for enforcement of SCAQMD SIP Rules,
for use in SCAQMD only.

M313-91 already appears as approved
SCAQMD method in EPA Region IX list.

Relevant Validation

EPA OAQPS METHOD 301

"Field Validation of Pollutant Measurement Methods From Various Waste Media"

What is EPA Method 301?

And what is it for?

- EPA Method 301 found in 40 CFR Part 63, Appendix A, Test Methods
- It is for the validation of alternatives to methods found in 40 CFR part 63, Appendix A, Test Methods
- Since Method 24 located in the same CFR section, M301 becomes a validation option

Options Within EPA Method 301

Comparing against a validated test method

Not applicable. M24 does not apply to low VOC concentrations.

Isotopic sampling

Not applicable. Requires mass spec quantitation.

Analyte (or surrogate) spiking

Surrogate spiking requires EPA acceptance.

Analyte Spiking

Six samples, each prepared in duplicate (unspiked) and in duplicate (spiked) for a total of 24 analyses

SAMPLE	UNSPIKED (M)		SPIKED (S)	
No 1	M_{11}	M_{21}	S_{11}	S_{21}
No 2	M_{12}	M_{22}	S_{12}	S_{22}
No i	M_{1i}	M_{2i}	S_{1i}	S_{2i}

Calculations per Method 301

BIAS

The bias of a candidate method is determined from the difference between the average spiked and unspiked concentrations, minus the prepared spike value

For sample i

$$d_i = ((S_{1i}-S_{21}) - (M_{1i}-M_{21})/2) - CS$$

where CS is the calculated spike concentration

Calculations per Method 301

PRECISION

The precision of a candidate method is determined from the standard deviation. The standard deviation may be estimated from paired data

$$SD = SQRT\ (\ \Sigma\ (S_i - S_m)^2\ /(n-1))$$

where S_m is the mean of the spiked concentrations

Additional

Sample stability

Method LOD

Subject to EPA approval

Questions?