

Absolute quantitative analytical method based on Curie-Weiss law "effective magnetic moment method"

Introduction

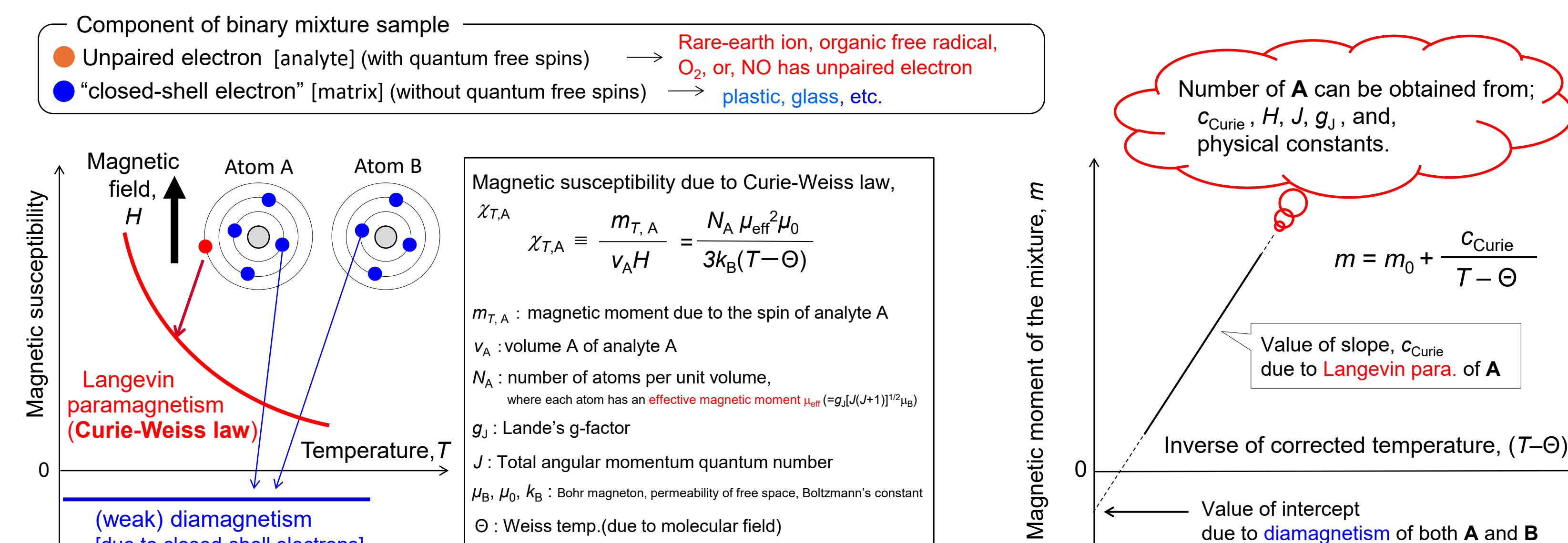
The gravimetry, coulometry, and dew-point depression, are recognized as the primary direct methods for amount-of-substance in the ISO Guide 35:2006. These methods have the highest quality in the metrological traceability chain and can measure the fraction of unknown substances without any reference to a standard. In this study, an absolute quantitative analytical method "the effective magnetic moment method" has been proposed. The "effective magnetic moment method" based on Curie-Weiss law can directly measure number of free spins of unpaired electrons, in a diamagnetic matrix. Examples of unpaired electrons are rare-earth ions, free radicals, and so on. In this presentation, principle, experimental method and applications of the effective magnetic moment method will be presented. As the examples of applications, quantification of rare-earth oxide, accurate purity analysis of stable free radical reagents, and radiation chemical yield of irradiated alanine dosimeter will be shown in this poster session.

Table. Features of primary direct methods for amount-of-substance and "effective magnetic moment method"

	Primary direct methods			(4)"effective magnetic moment method" (This work)
	(1) gravimetry	(2) coulometry	(3) freezing point depression method	
Academic field	Inorganic chemistry	Electro-chemistry	Thermo-dynamics	Magnetism
Scientific law	—	Faraday's law	Van't Hoff equation	Curie-Weiss law
Analyte	Inorganic salt	Metallic elements	High-purity organic liquid	Atoms with unpaired electrons (matrix of sample is diamagnetic)
Equipment	Balance	Titration system	Calorimeter	Magnetometer (ex. SQUID)

Principle

Utilization of differences in the temperature dependences of Langevin paramagnetism and diamagnetism



Analytical example (1) Powder mixture of gadolinium oxide(Gd₂O₃) in silicon dioxide(SiO₂)

Sample is mixture with a known concentration by gravimetric blending method.

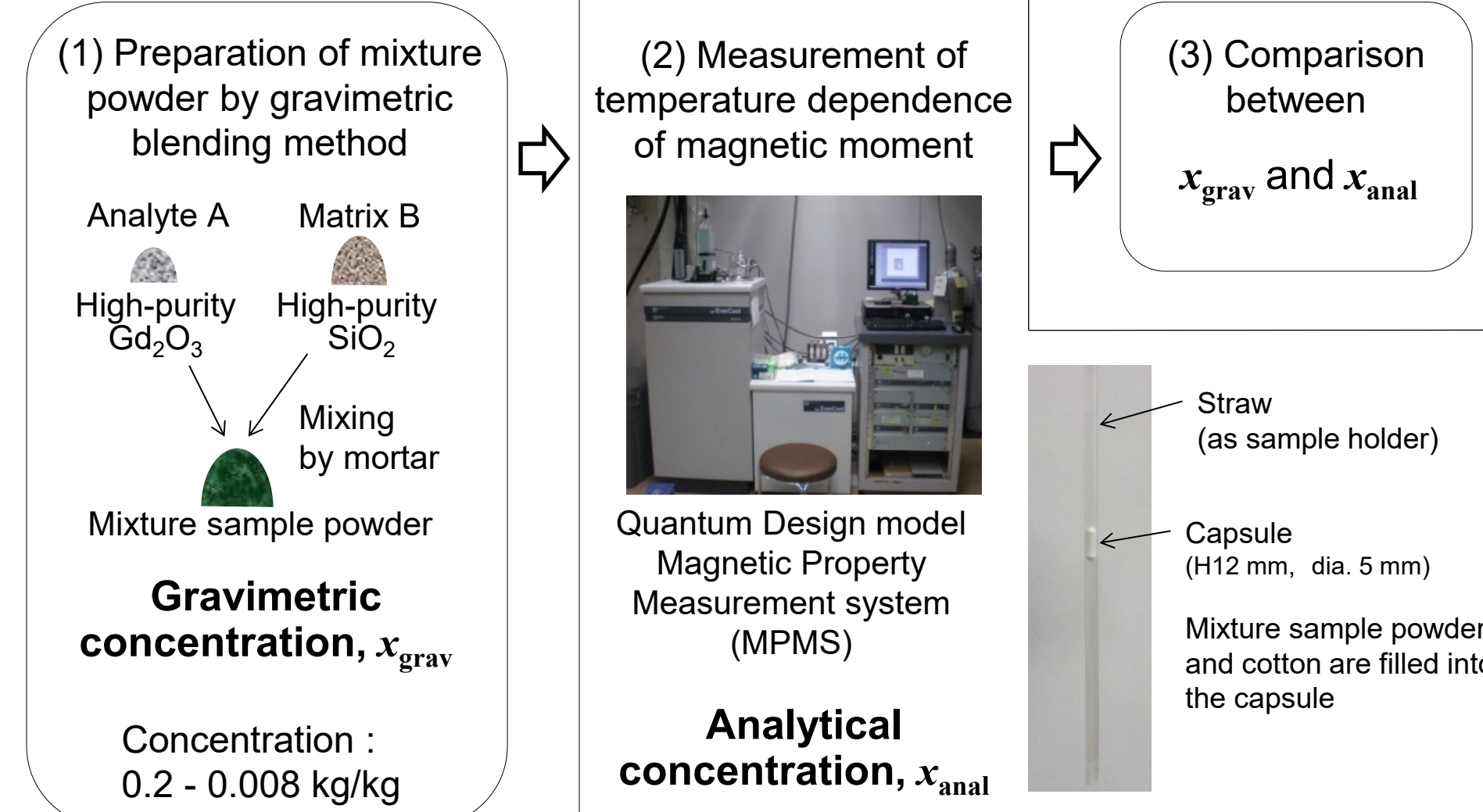


Fig. Procedure of experimental validation on the principle of "effective magnetic moment method"

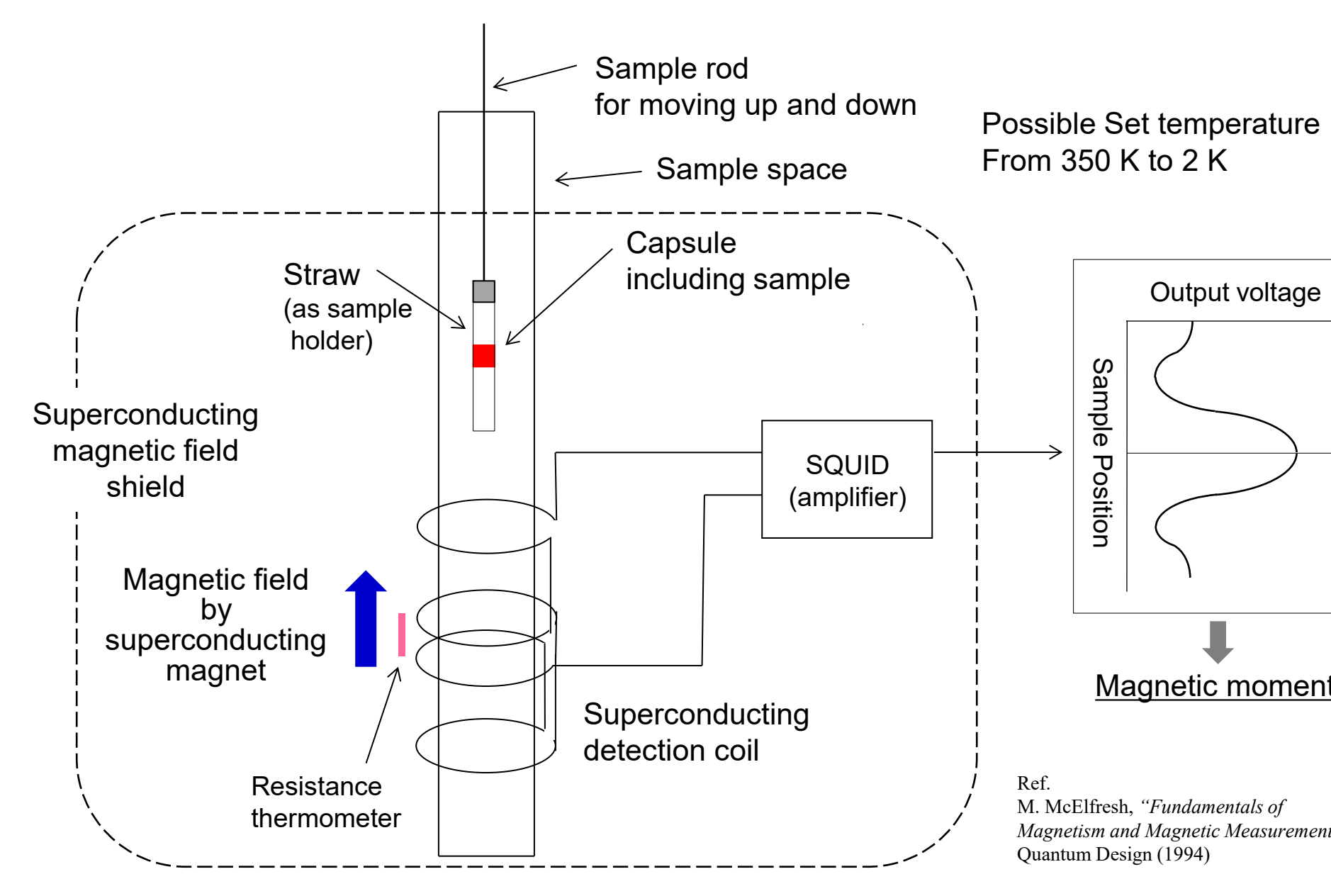
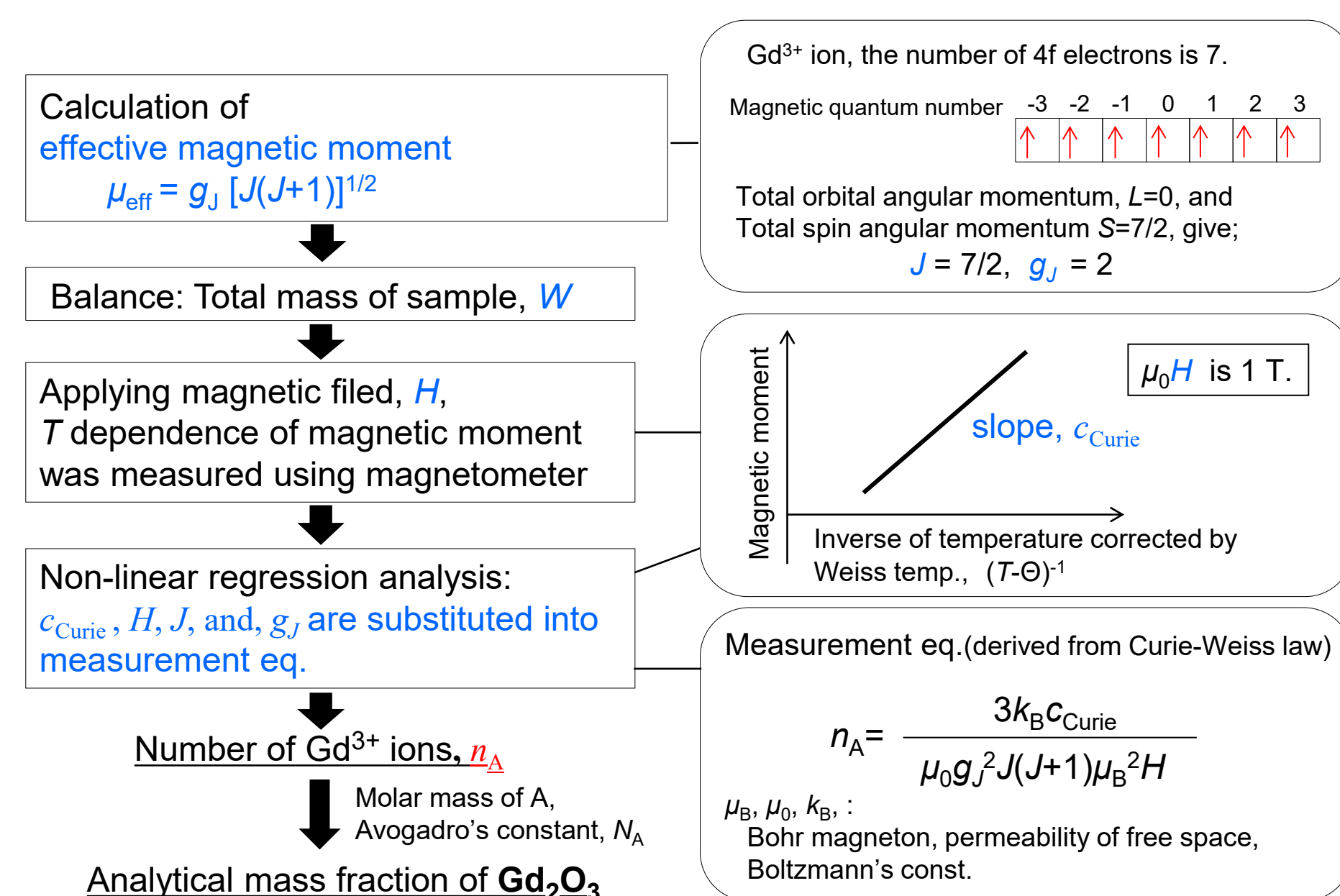


Fig. simple schematic illustration of SQUID magnetometer used for temperature dependence measurement of magnetic moment

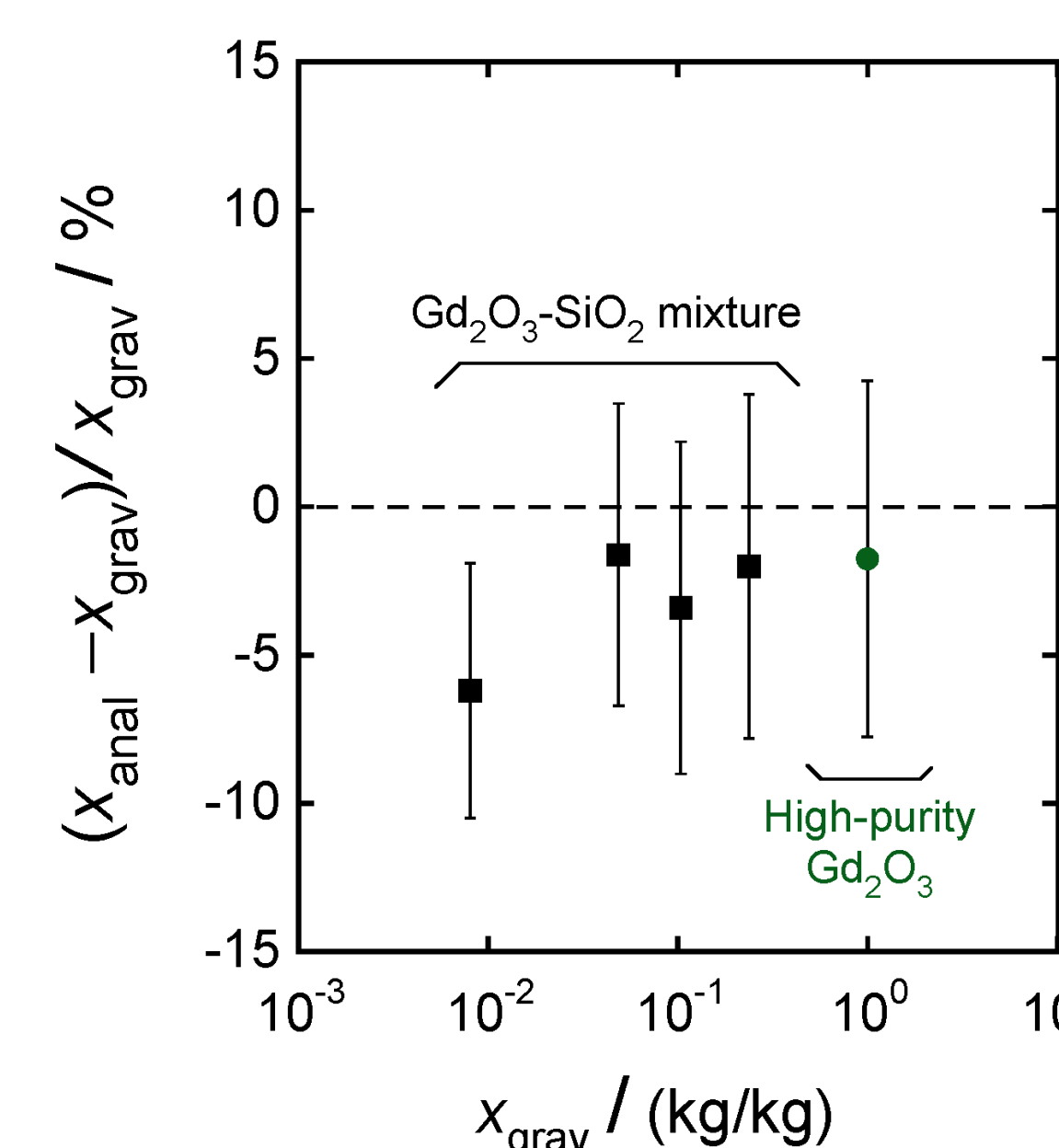


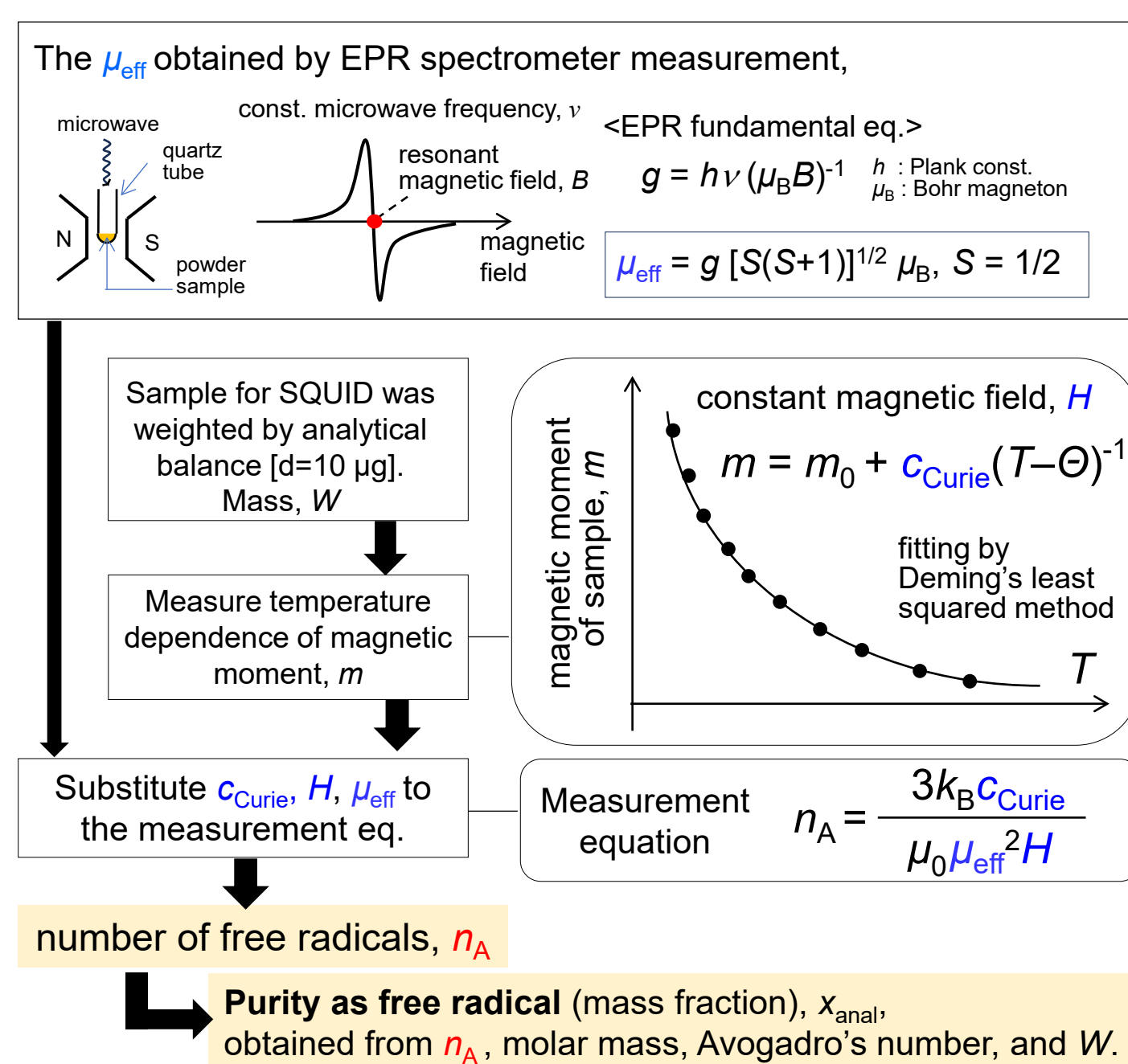
Fig. simple schematic illustration of SQUID magnetometer used for temperature dependence measurement of magnetic moment

The x_{grav} and x_{anal} consists with each other in mass fraction of 100% to 8%

This method is appropriate for purity analysis, or, quantification of large mass fraction mixture

Ref.) N. Matsumoto, T. Shimosaka, Accred. Qual. Assur. 20, pp.115-124 (2015)

Analytical example (2) Pure free radical reagents



- This method can measure purity as free radical for stable pure free radical reagents.
- Relative uncertainty of the purity: 0.3% for 4HTB, 1.0% for TEMPOL, 1.5% for DPPH
- The purities of these reagents for each compound are different beyond their uncertainties.

Table. Results of purity as free radical of stable free radical reagents

Pure free radical reagent	Purity as free radical, x_{anal} (kg kg ⁻¹)	(ref.) Purity by manufacturer
4-hydroxy TEMPO benzoate (4HTB)	4HTB-A: 0.9919 ± 0.0030 4HTB-B: 0.9830 ± 0.0029	Approx. 1% difference 98.5% by GC 99.2% by GC 99.3% by titration
TEMPOL	TEMPOL-A: 1.0073 ± 0.0097 TEMPOL-B: 0.9861 ± 0.0095	Approx. 2% difference 99.5% by GC 97%
DPPH	DPPH-B: 0.995 ± 0.015 DPPH-C: 0.835 ± 0.012	Approx. 16% difference 97.1% by HPLC (no information)

Ref.) N. Matsumoto, N. Itoh, K. Yamasaki, Anal. Chem. 94, pp.12595-12603 (2022)

Analytical example (3) Alanine dosimeter

Ref.) H. Yamaguchi, N. Matsumoto, H. Takahashi, Radiation Measurement, 154, 106754 (2022)

Table. Comparison of G-value or the number of radicals per mass for 101 kGy irradiated alanine

Author (Year)	G-value, $\mu\text{mol} \cdot \text{J}^{-1}$	Uncertainty	The number of radicals per mass for dose of 101 kGy, kg ⁻¹	Difference to this work
Gottschall and Tolbert (1968)	0.34	NA	2.08×10^{22}	8.7%
Regula and Deffner (1982)	0.31	NA	1.89×10^{22}	1.2%
Parita et al. (1989)	0.215	30%	$(1.30 \pm 0.39) \times 10^{22}$	32%
Nakagawa et al. (1993)	0.28	10%	$(1.70 \pm 0.17) \times 10^{22}$	11%
Stuglik and Sadio (1996)	0.36	30%	$(2.21 \pm 0.66) \times 10^{22}$	15%
This work	0.31	3.0% (k=1)	$(1.91 \pm 0.05) \times 10^{22}$	-

sample: alanine pellet (diameter 5mm, height 3mm) irradiated by high-dose gamma ray of 101 kGy

$$\text{Radiation chemical yield (G-value)} = \frac{\text{Amount-of-substance of radicals per unit mass}}{\text{absorption dose}}$$

Relative quantitative analysis of alanine dosimeter by using ESR spectrometer.
ex. Nakagawa et al.(1993)
Standard solution of nitroxyl radical diluted by toluene for calibration of the ESRspectrometer)

(This work) Absolute quantitative analysis by effective magnetic moment method.

Other possible analytical example (under study)

Nitrogen monoxide (NO) gas also has unpaired electron.

However, it is difficult to measure magnetic moment of gas by the SQUID magnetometer.

Then, a magnetic balance for measuring magnetic susceptibility is under construction, for trial of purity analysis of pure nitrogen monoxide gas.

Acknowledgement

SQUID, EPR

· AIST Nano Processing Facility, supported by the Nanotechnology Platform Program of the Ministry of Education, Culture, Sports, Science, and Technology, Japan, grant number: JPMXP09F21009291.
· Institute for Molecular Science, National Institutes of Natural Sciences, supported by the Nanotechnology Platform Program of the Ministry of Education, Culture, Sports, Science and Technology, Japan. (JPMXP09S21MS1016)
· Dr. K. Mizugaki, Dr. K. Morimoto, Dr. M. Nishikata, Dr. M. Suzuki (GREEN/AIST)

Program for Deming's least squared method

Dr. T. Shimosaka (NMIJ/AIST)

CHN analysis

Dr. N. Itoh, Ms. M. Matsuo (NMIJ/AIST)

¹H-NMR measurement

Dr. K. Yamasaki, Dr. H. Shimizu (NMIJ/AIST)

Alanine dosimeter measurement

Dr. H. Yamaguchi (NMIJ/AIST)

Others

JPSJ KAKENHI, grant numbers: 24750077, JP17K05918 and 21H01972.