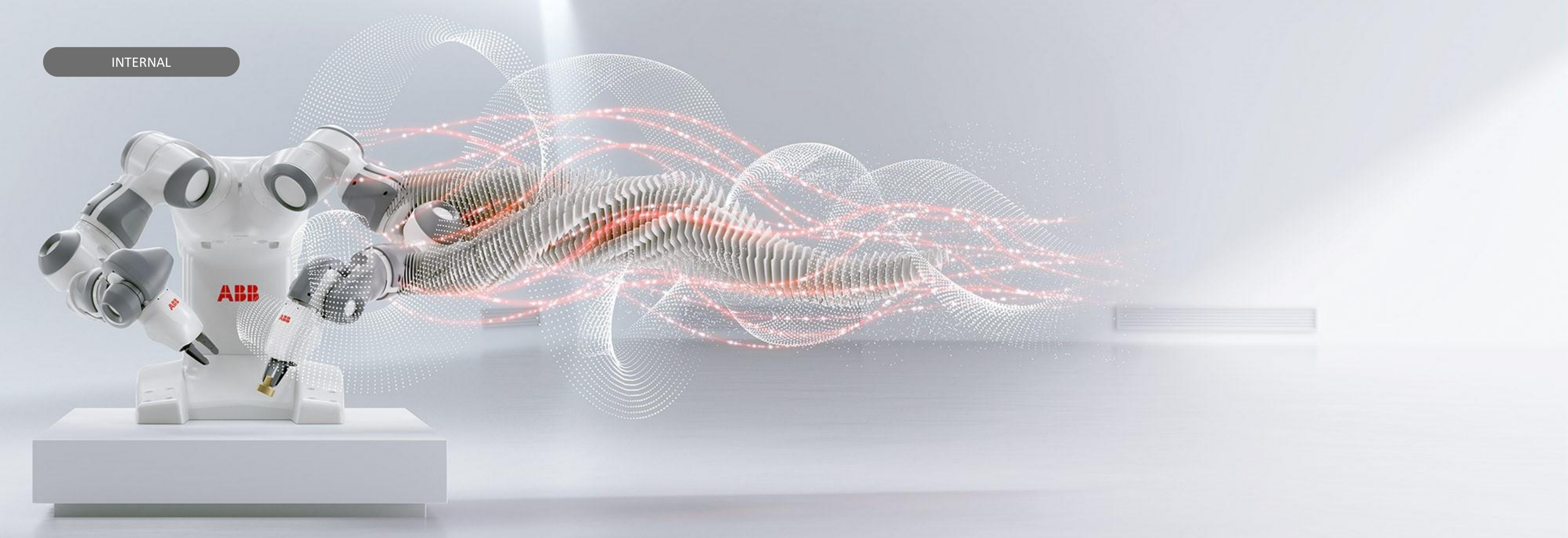
INTERNAL



On the noise floor of constant temperature thermal conductivity detectors

SENSORDEVICES 2024

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Antoine Riaud received his PhD in acoustics, microelectronics, and telecommunications from Lille University (France) in 2017. He then completed a postdoc at Paris Descartes University. From 2018 to 2022, he worked as an associate professor at Fudan University (Shanghai, China). Since 2022, he has joined the sensing and analytics team at the ABB Corporate Research Center in Switzerland.

His research interests include microsystems and microfluidics, sensing technologies and data analytics. He has authored or co-authored over 37 peer-reviewed journal publications in these fields and holds 6 issued or pending EU/international patents

Gas chromatography

Thermal conductivity detector

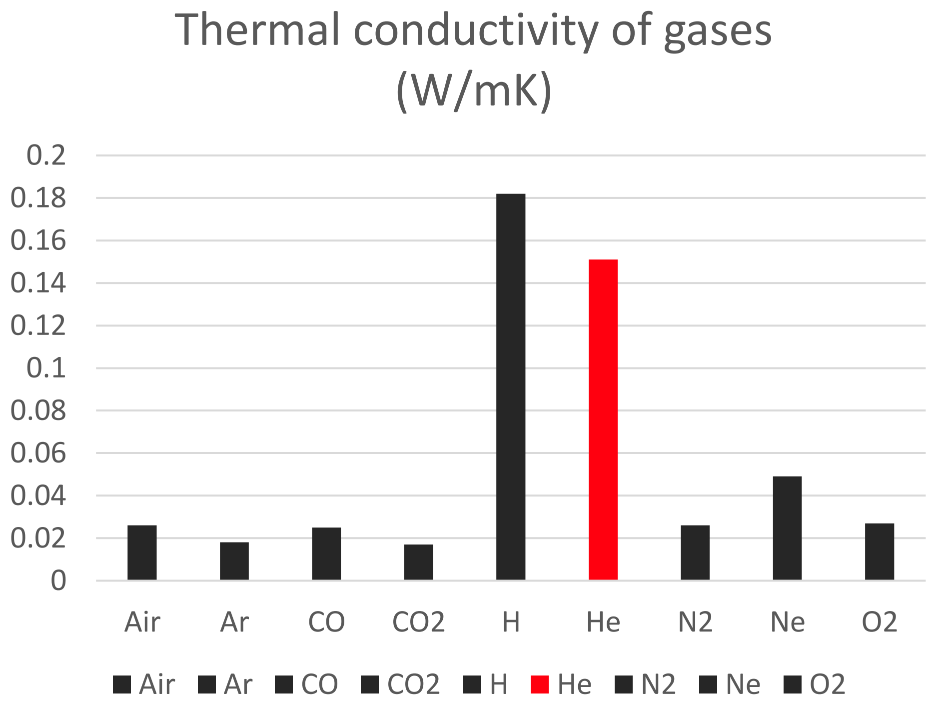
$$k$$

- Independent of pressure
- Highly contrasted between light gases (H, He) and other gases

For a mixture of gases 1 and 2, with x_2, x_2 the molar fractions of each gas:

$$k_{mix} = \sum_i \frac{k_i(T)}{1 + \sum_{j \neq i} \phi_{ij} \frac{x_j}{x_i}}$$

ϕ_{ij} Interaction term, very weakly dependent on temperature



Thermal conductivity depends only on temperature & molar fraction

Thermal conductivity detector

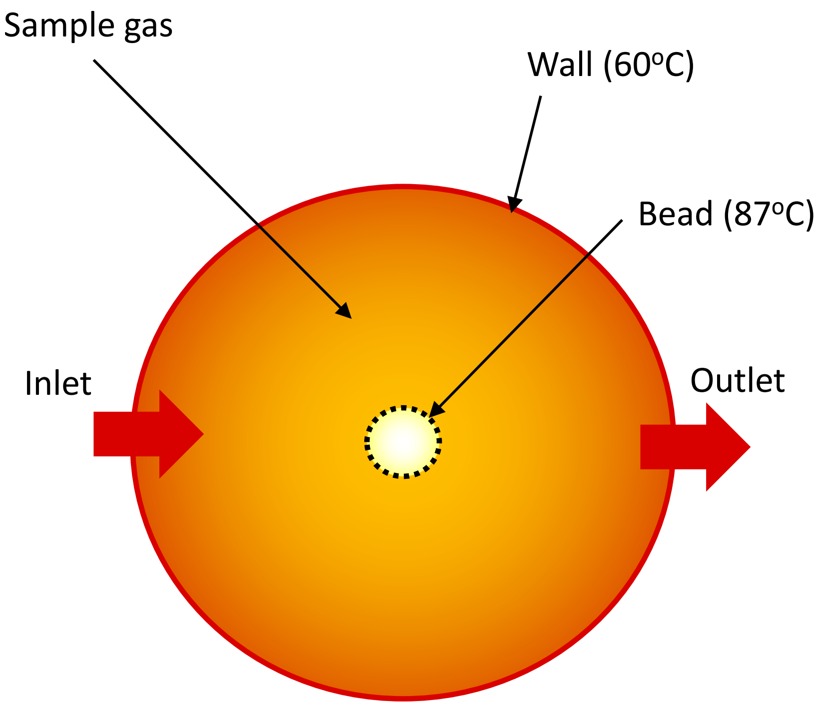
Applications

Gas chromatography (measure the concentration of separated components)

Leak detection (of Helium & Hydrogen)

Thermal conductivity detector

Principle



Thermal conductivity

Heat rate

Bead diameter

$$\dot{Q} = k_{mix} \frac{\pi}{2} \delta \Delta T$$

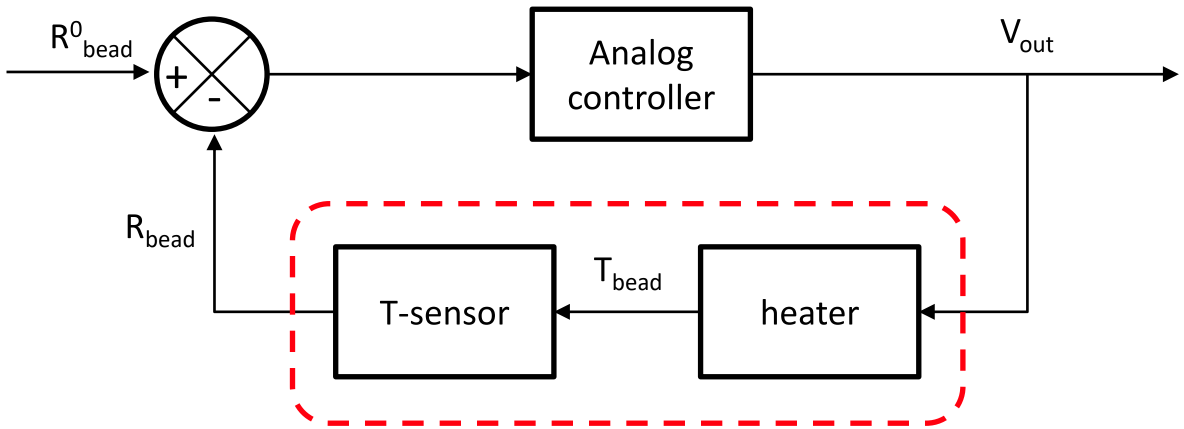
Temperature difference

- Independent of the flow velocity
- Independent of gas pressure
- Wall & bead temperature are tightly regulated

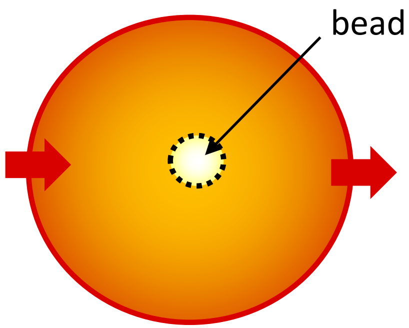
Thermal conductivity is a <u>material property</u> that measures the transfer of heat by conduction

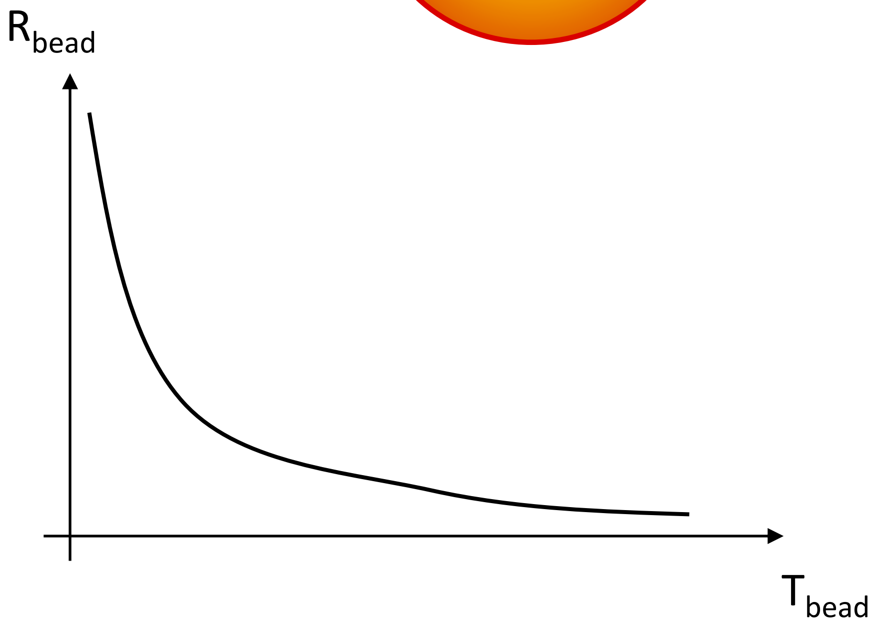
Constant temperature TCD

Regulation of the bead temperature



Negative temperature coefficient (NTC) resistor

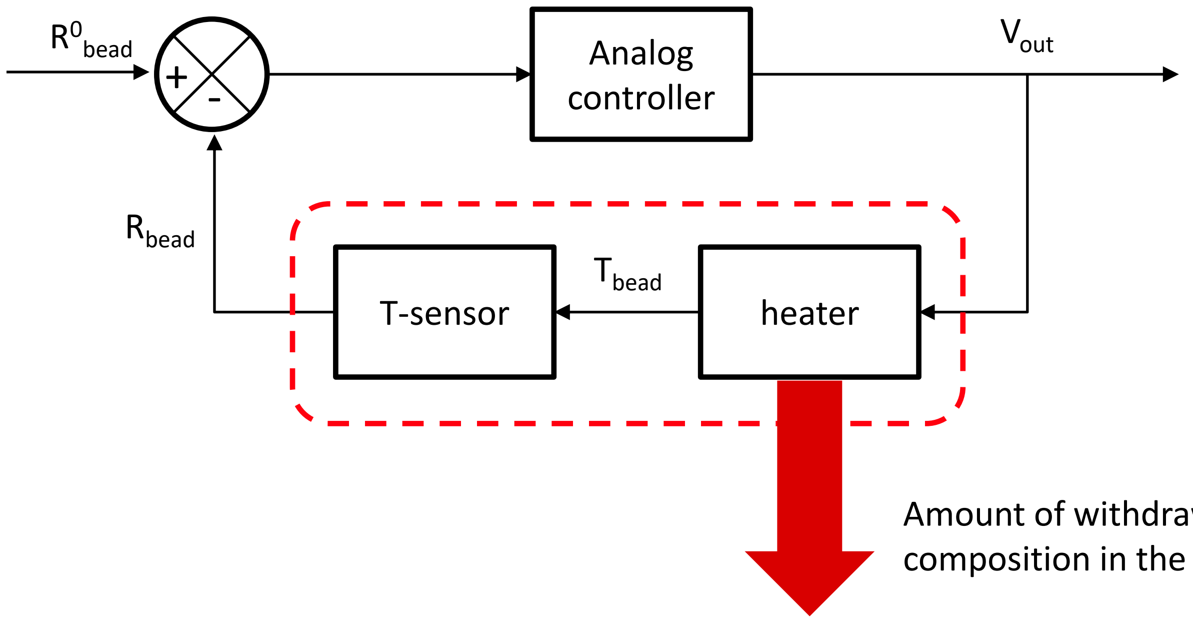




NTC: 2-in-1 device that measures temperature (resistance variation) and creates heat (Joule heating)

Constant temperature TCD

Regulation of the bead temperature



Amount of withdrawn heat depends on gas composition in the detector cell

The sensor measures the amount of heat needed to maintain the bead at the temperature setpoint

Noise analysis

Trace gas

$$k_{mix} \approx k_{He}\left[1 + \underbrace{x_i\left(\frac{k_i}{k_{He}}\frac{1}{\phi_{i,He}} - \phi_{He,i}\right)}_{\sim 10^{-6}}\right]$$

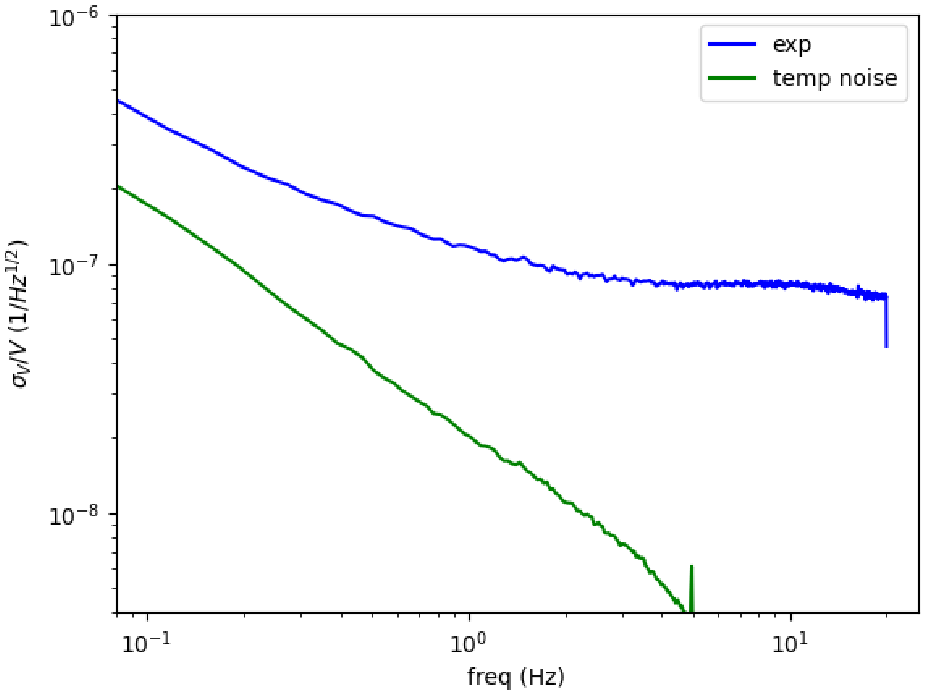
$$U^2 = k_{mix} R_{NTC} \frac{\pi}{2} \delta \Delta T$$

$$2\frac{dU}{U} = \frac{dk_{mix}}{k_{mix}} + \frac{d\Delta T}{\Delta T}$$

Output voltage/baseline [measurement]

Thermal conductivity variation /baseline [signal]

Temperature fluctuations [noise]



The temperature does not explain well the sensor noise

Noise analysis

Trace gas

$$k_{mix} \approx k_{He}\left[1 + \underbrace{x_i\left(\frac{k_i}{k_{He}}\frac{1}{\phi_{i,He}} - \phi_{He,i}\right)}_{\sim 10^{-6}}\right]$$

$$U^2 = k_{mix} R_{NTC} \frac{\pi}{2} \delta \Delta T$$

$$2\frac{dU}{U} = \frac{dk_{mix}}{k_{mix}} + \frac{d\Delta T}{\Delta T} + \frac{d\delta}{\delta} + \frac{dR_{NTC}}{R_{NTC}}$$

Output voltage/baseline [measurement]

Thermal conductivity variation /baseline [signal]

Bead diameter error/bead diameter [noise]

Resistor error/baseline [noise]

Any resistor has:
- 1/f noise (flicker noise)
- Thermal noise (white) <- our noise is white

R_{NTC} ~ 3 kΩ

$$U_{th} = \sqrt{4k_B TR} \sim 7.4 \frac{nV}{\sqrt{Hz}} \sim 0.012 \frac{counts}{\sqrt{Hz}}$$

Expected thermal noise is 100 times smaller than the experiment (1.53 counts/sqrt(Hz))

Then that leaves only the 1/f noise…

Excess 1/f noise:

Quantification using Hooge's law

Resistance variance/Hz

Hooge coefficient

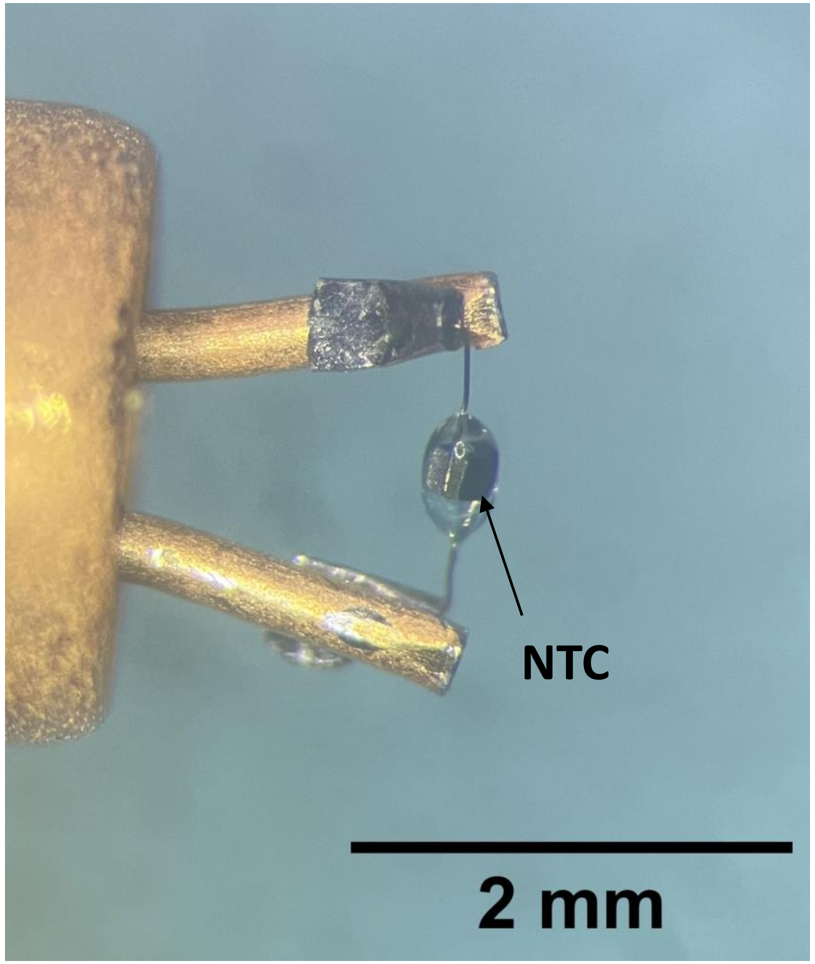
$$\frac{S_{RR}}{R^2} = \frac{\alpha_H}{N\Omega f}$$

Resistance mean value

Carrier density

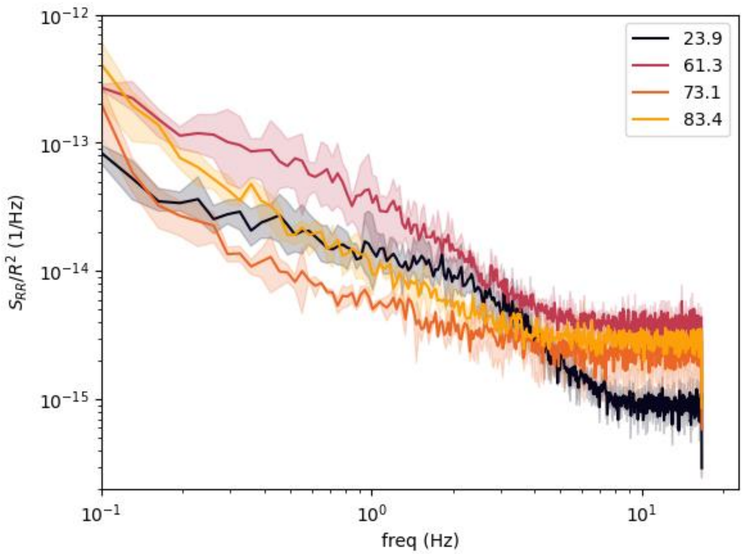
Resistor volume

frequency

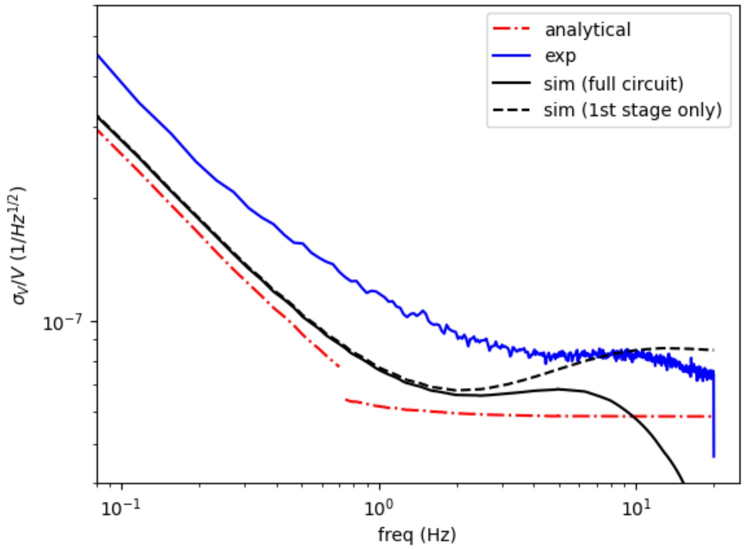


Noise model

High fidelity electro-thermal model

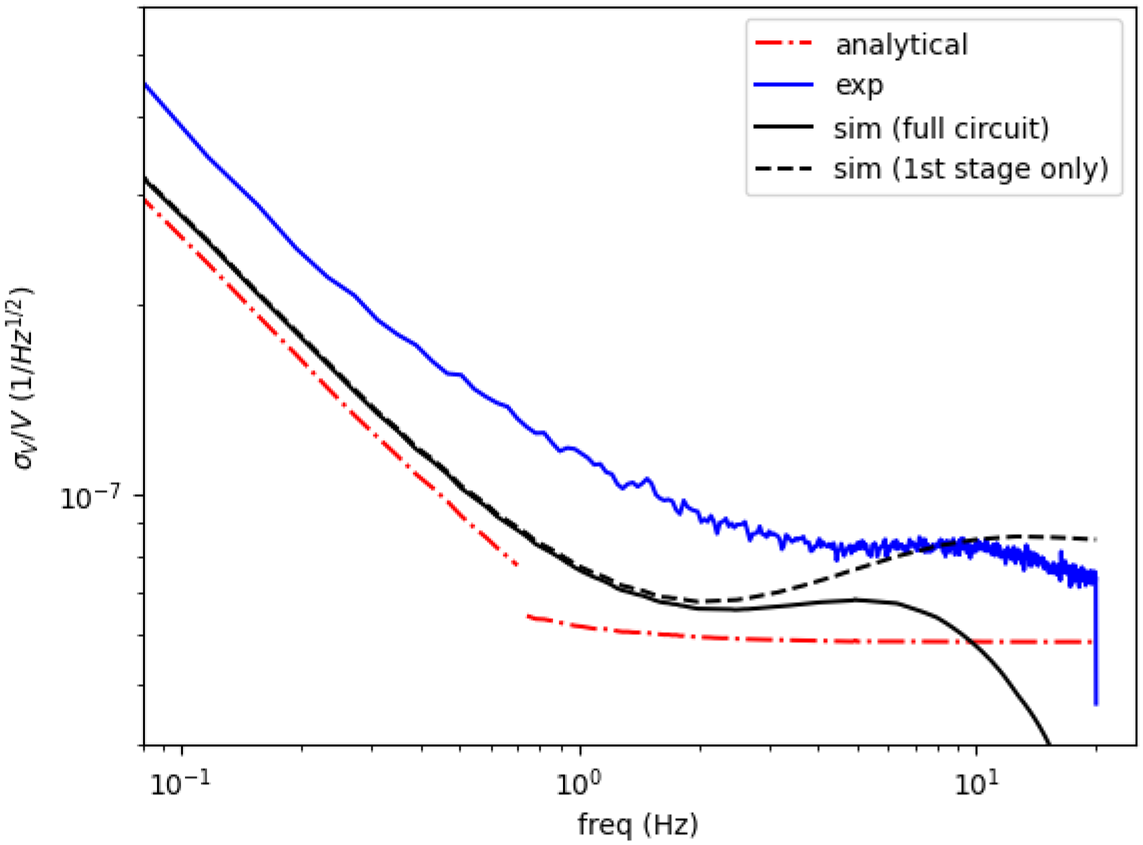


Experimental NTC noise spectra at various bead temperatures (°C)



Experimental TCD noise spectra

Results



analytical
exp
sim (full circuit)
sim (1st stage only)
$\sigma_V/V\ (1/Hz^{1/2})$
10^{-7}
10^{-1}
10^{0}
10^{1}
freq (Hz)

Noise model

Asymptotic analytical model

Assume bead temperature perfectly regulated

=> The bead temperature changes to cope with the noisy resistance

$$dR = \frac{\partial R}{\partial T}(T^* - T) + n = 0$$

With the power spectral density of *n* given by Hooge's noise expression:

$$\mathrm{S(n)} = \frac{S_{RR}}{R^2} = \frac{\alpha_H}{N\Omega f}$$

This changes the voltage on the bead:

$$\frac{V^{*2}}{R} = \frac{T^* - T_w}{Z}$$

Wall temperature

Thermal impedance of the bead

Low-frequency asymptote:

$$\frac{S_{VV}}{{V_b}^2} \approx \frac{2\pi\alpha_H}{N\Omega\omega}\left|\frac{T^2}{2\beta(T - T_w)}\right|^2$$

High-frequency asymptote:

$$\frac{S_{VV}}{{V_b}^2} \approx \frac{2\pi\alpha_H}{N}\left|\frac{T^2}{2\beta(T - T_w)}\frac{3{r_b}^2\epsilon}{2\pi\kappa_g r_N}\right|^2$$

Minimization of the noise

Sketch of a perfect bead

Low Hooge coefficient

T = 2T$_w$

Small bead (less glass)

High bead effusivity

$$\frac{S_{VV}}{{V_b}^2} \approx \frac{2\pi\alpha_H}{N} \left| \frac{T^2}{2\beta(T - T_w)} \frac{3{r_b}^2\epsilon}{2\pi\kappa_g r_N} \right|^2$$

High charge carrier density

High temperature coefficient

High ambient fluid thermal conductivity

Larger NTC

Independent of the circuit, mainly depends on the NTC geometry & material

ABB