

**Title:** High-performance fixed-bed *in situ* mass analyzer - ISMA

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### Abstract

We demonstrate a newly developed high-performance fixed-bed reactor combined with an *in situ* mass analyzer (ISMA). The ISMA is particularly relevant to sub-second time-resolved studies where mass changes occur due to e.g., chemical reactions and process conditions such as choice of solid, temperature, gas atmosphere and pressure. The mass is determined from the optically measured oscillation frequency of a quartz element, yielding a mass resolution below 10 micrograms – typically 2-3 micrograms – for samples up to ca. 500 mg. By placing the quartz element and optical sensor inside stainless steel pipes, and providing heat from the outside, the instrument is applicable up to approximately 62 bar and 700 °C. By surrounding this core part of the instrument with a suitable feed system and product analysis instruments, in combination with computer control and logging, time-resolved studies are enabled. The instrument with surrounding feed and product analysis infrastructure is fully automated. Emphasis has been put on making the instrument robust, safe, operationally simple, and user-friendly. We demonstrate the ISMA instrument on selected samples.

### Introduction

A variety of important phenomena are associated with mass changes, e.g., chemical reactions, adsorption, desorption, and decomposition. Important information can be obtained from time-resolved *in situ* mass studies, and to this end, we have developed a well-suited high-performance instrument labelled *in situ* mass analyzer (ISMA).

Fixed-bed reactors are frequently used in laboratory scale studies<sup>1,2</sup>, on industrial scale<sup>3,4</sup>, and they are well-suited for modelling<sup>5</sup>. Mass determination by frequency measurements is also known. For example, the quartz crystal microbalance (QCM) has been successfully applied to studies over a broad range of areas, e.g., batteries<sup>6</sup>, electrode surfaces<sup>7</sup>, biosensors<sup>8</sup>, and gas sensors<sup>9</sup>. Furthermore, QCM is key to recently developed instruments<sup>10,11</sup>. By combining QCM and ion beam analysis, an *in situ* study of thin film growth was recently carried out<sup>12</sup>.

In the early 1980s, Rupprecht & Patashnick Co. Inc. developed instrumentation based on the tapered element oscillating microbalance (TEOM) technology. It was originally developed for space related programs but found a larger application base in particle measurement and air quality monitoring in mining industry and similar<sup>13,14</sup>. Based on the same working principle, and targeting R&D work within catalysis, adsorption, coking, kinetics studies and similar, they also developed the TEOM 1500 Reaction Kinetics Analyzer. This instrument was available from approximately 1985 until support ceased in 2009. The original instrument TEOM 1500, also referred to as the R&P TEOM 1500 Pulse Mass Analyzer (PMA), was a powerful instrument able to produce unique data albeit with some experimental challenges.

The TEOM is described in several articles focused on chemical engineering, heterogenous catalysis, reaction kinetics, diffusion and adsorption. For instance, Hershkowitz and Madiara studied adsorption, reactions, and coke formation on La<sup>3+</sup>Y zeolite<sup>15</sup>, Chen *et al.* reported on catalyst deactivation during ethene oligomerization over H-ZSM-4<sup>16</sup>, coke formation and its effect on transport and adsorption in zeolites<sup>17</sup>, discussed how the coke formation influences on the selectivity for zeolite catalysts<sup>18</sup>, and reviewed the field<sup>19</sup>. Furthermore, Perez-Ramirez *et al.* evaluated catalytic performance, deactivation, and regeneration in order to develop a cyclic process for continuous production of propene using Fe-zeolites<sup>20</sup>, whereas Rebo *et al.* studied Pt-Sn catalyst deactivation during propane dehydrogenation<sup>21</sup>. Zhu *et al.* reported on isotherms and kinetics of butane adsorption on Kureha activated carbon<sup>22</sup>, adsorption of light alkanes in silicalite-1<sup>23</sup>, and hydrodechlorination over Pt-Cu/C catalyst<sup>24</sup>. Olafsen *et al.* applied TEOM in combination with other techniques to study CO<sub>2</sub> reforming of methane and propane on Ni-catalysts<sup>25</sup>, and Gomm *et al.* studied coke deposition on zeolite catalysts with different pore systems<sup>26</sup>. Mishakov *et al.* studied the non-catalytic reaction between CF<sub>2</sub>Cl<sub>2</sub> and MgO<sup>27</sup>. Most recently, TEOM was used to study the internal and external acidic properties on zeolites<sup>28</sup>.

Since *in situ* mass measurements are important, we decided to revive and improve on the TEOM concept. Herein, we describe a new instrument developed by SINTEF Industry. We emphasize ISMA's high-performance, and important improvements compared to the original TEOM 1500, e.g., resolution, optics and signal handling, long-term stability at elevated temperature and pressure, user friendliness, safety, and automatization, and we provide non-limiting examples from its use. The new instrument is referred to as an *In Situ* Mass Analyzer, ISMA.

### Working principle

For a cantilever fixed at one end, and assuming that all mass is located at the free-moving end, the mass is inversely proportional to the square of the oscillating frequency. Equation 1 describes the relationship between the changes in mass and oscillating frequency, respectively.

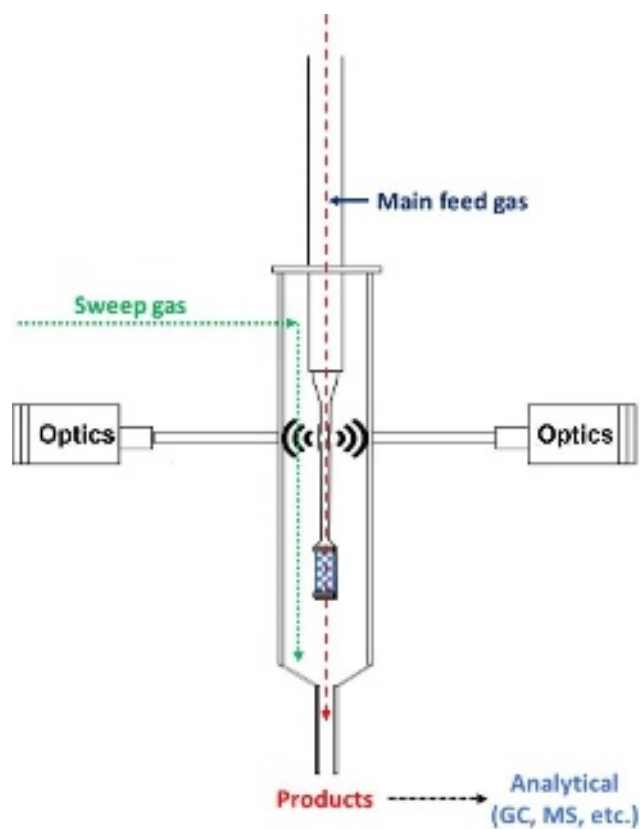
$$\Delta m = m_2 - m_1 = k \times \left( \frac{1}{f_2^2} - \frac{1}{f_1^2} \right) \quad (\text{Equation 1})$$

where  $\Delta m$  is the mass change,  $f_1$  and  $f_2$  are the frequencies at time 1 and 2, respectively, and  $k$  is the force constant specific for each oscillator. The mass change can thus be determined from frequency measurements.

The overall ISMA concept is an instrument where a solid sample is positioned inside a vertically oriented tube (Figure 1). The tube is fixed in the upper end and allowed to freely oscillate in the lower end where the sample is located. After the oscillations have been initiated, high-quality frequency measurements under controlled experimental conditions and stable oscillations allow the user to

accurately *in situ* monitor the mass with time. The reactor is constructed from a hollow quartz tube where the sample is loaded into the enlarged bottom of the tube. The upper end of the tube is tightly screwed to the core body. The reactor is initially set to oscillate, and the frequency is measured using a Light Emitting Diode (LED) and a phototransistor. This readout frequency signal is passed through a processing unit that sends a control signal further on to a frequency motor that maintains the oscillation at the correct frequency. When the sample mass changes due to the sample conditions, so does the oscillating frequency. The concept is sketched in Figure 1.

The sample is positioned in the middle of a heated zone where the temperature profile is uniform. An outside sweep gas serves several purposes: transport of products through the system, protecting the optical parts from feed and product, and avoiding condensation in downstream parts of the system. The construction ensures that the feed gas flows through the sample so that fixed-bed conditions are achieved, as was the case for TEOM 1500. This is a major advantage compared to microbalances where significant bypass of the gas is of considerable concern. High mass resolution and a short response time are favorable features of the new ISMA instrument. Some key features of the new ISMA are: rigid vibrational frame system, no tuning required during tests, robust electronics and control, and no loss of track during tests. The well-defined light source and detector system ensures that no tuning is required.

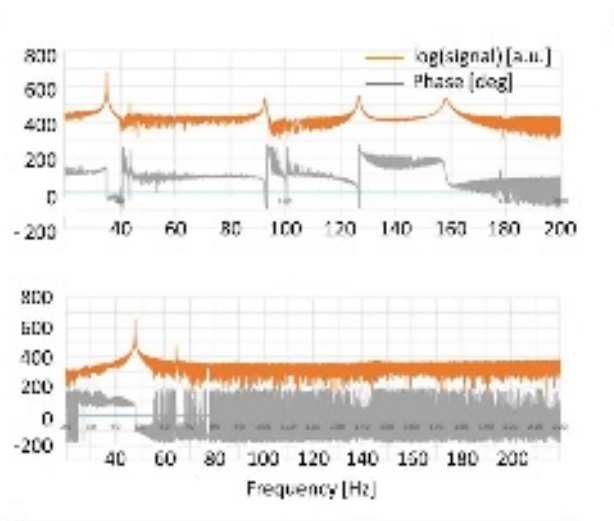


**Figure 1.** ISMA sketch. Heaters omitted for clarity. Not drawn to scale.

Frequency changes are due to both the mass-change in the sample, and any changes in the operating conditions, e.g., temperature, pressure, gas density, and atmosphere in the reactor. Any user who seeks information on only the mass changes that take place in the sample, should therefore run blank

experiments to correct for the frequency changes, and thereby calculated mass changes, driven by the operating conditions.

A significant effort was made to eliminate parasitic resonances stemming from other resonances in the set-up. The goal was to keep the interval 40 – 100 Hz free from unwanted resonances. It is important that the element has a clean excitation of only one resonance mode. In addition to the initial parasitic modes from other mechanical resonances, it also turned out that the initial excitation of the element was a combination of translation and angular excitation. By exciting the element by purely translating the base of the element back and forth, a very sharp resonance was obtained. Furthermore, a new element that has a more distinct ovality than used in the earlier TEOM instrument was developed, and consequently modes transverse to the excitation have a more distinctly different frequency. The improvements are illustrated in Figure 2.



**Figure 2.** Measured amplitude (orange) and phase (grey). Upper: intermediate results. Lower: final result with an element oscillating in its fundamental mode at 48 Hz. At 64 Hz we find the transverse mode of the element. The transverse mode is visible because it is difficult to align the element 100%.

Tracking of the resonant frequency is done by measuring the phase of the measured oscillation relative to that of the excitation. Initially, the approximately correct resonance frequency should be found. A light knock on the instrument sets the element in oscillations. The measured signal goes through an FFT, and the frequency content of the signal is displayed. The knock is done by a voice coil motor. Then, the excitation is set close to the resonance frequency. The signal is recorded, and the phase and amplitude are measured and displayed. Now the correct phase is found by iteration. The correct phase is where  $d(\text{phase})/df$  is at its highest. The instrument is now set to measure and track the phase. The element has shown insignificant drift in the phase at resonance, but it is possible to set a second phase at a higher temperature and interpolate.

The fundamentals of the operation is given by the differential equation for a forced damped vibration. By measuring phase and amplitude for several frequencies around the resonance one can accurately determine the resonance frequency. As can be seen there is a linear relationship between frequency and phase in an interval around the resonance, so to find the exact frequency is not necessary. Low damping is important, so the active material must be packed to minimize friction losses. Furthermore, the element must be well attached to its metal base and the base must be fixed in the instrument.

## Instrument description

Stable quartz element oscillations are maintained by oscillations of the ISMA core (Figure 3). The core is separated from the rest of the unit by four rubber feet, which also minimizes the influence of outside vibrations. Standard sized tubes and parts, e.g., Swagelok components and connections, are used throughout the instrument because it simplifies replacement and ensures compatibility. Fragile metal/glass junctions are not used. The quartz element allows high performance and stability at high temperatures. The complete vibrational structure, the reactor and the heating system have been redesigned. New software utilizing modern real-time automation hardware has been created and implemented, including several aspects of error, alarm, and safety handling. Analytical control has also been implemented as part of the automation.

More robust electronics and procedures for controlling the vibrating system have resulted in ISMA being much less sensitive to external disturbances compared to TEOM. Running the core control logic of the oscillation system on software running on a FPGA chip, independent of all events that might occur on the main computers operating system, made the feedback control very insensitive to variations in signal or frequency shifts. The whole system was constructed symmetric in terms of weight, so there was no need for any adjustable counterweight. The first ISMA was started up in 2017, and so far, the tracking of the frequency has always kept up, the frequency has not been lost once in these years. The only time we observed a loss of frequency was when the chemistry produced enough coke on the stainless-steel wall to clog the reactor. The issue was solved by passivating the stainless-steel surface by Silcolloy 1000, and it has not reoccurred.

The accuracy of the new ISMA is typical 0.01 mg or lower. It can operate up to 62 bar and 700°C, on sample size typically 50 – 500 mg, with options to increase it up to 1000 mg. The feed-system is tailor-made according to the chemistry, whether liquid feed is needed and hence an evaporator, if both reducing and oxidizing gases are to be fed to the reactor etc.

## Safety issues

The safety built into the system includes, but is not limited to:

- Safe state definition of all controls defined by operator, enforced when Emergency button is selected in the software.
- Normally closed flow and pressure controls on the inlet side, and Normally Open flow and pressure units on the outlet side.
- Inert flushing of system activated if power is lost.
- High limits for pressure controlled by safety relief valves.
- High temperature limits handled by independent control loops.
- Forced inert flushing when switching between reducing and oxidizing gases.
- Temperatures and flow do not resume when power is restored until manually reset (latching)

The automation software that controls the complete feed-system, the reactor and the analytical (typically gas chromatograph) is created in LabVIEW from National Instruments, as was the original TEOM 1500. The complete system is visualized in the main Graphical User Interface (GUI), with direct access to all setpoints for temperature, flows, pressure, valve position etc. All process parameters are logged in charts trending data for the last 10 days, updated every 15<sup>th</sup> second. For unattended testing a dedicated editor (MethodBuilder) is used to plan all setpoints on all steps in a

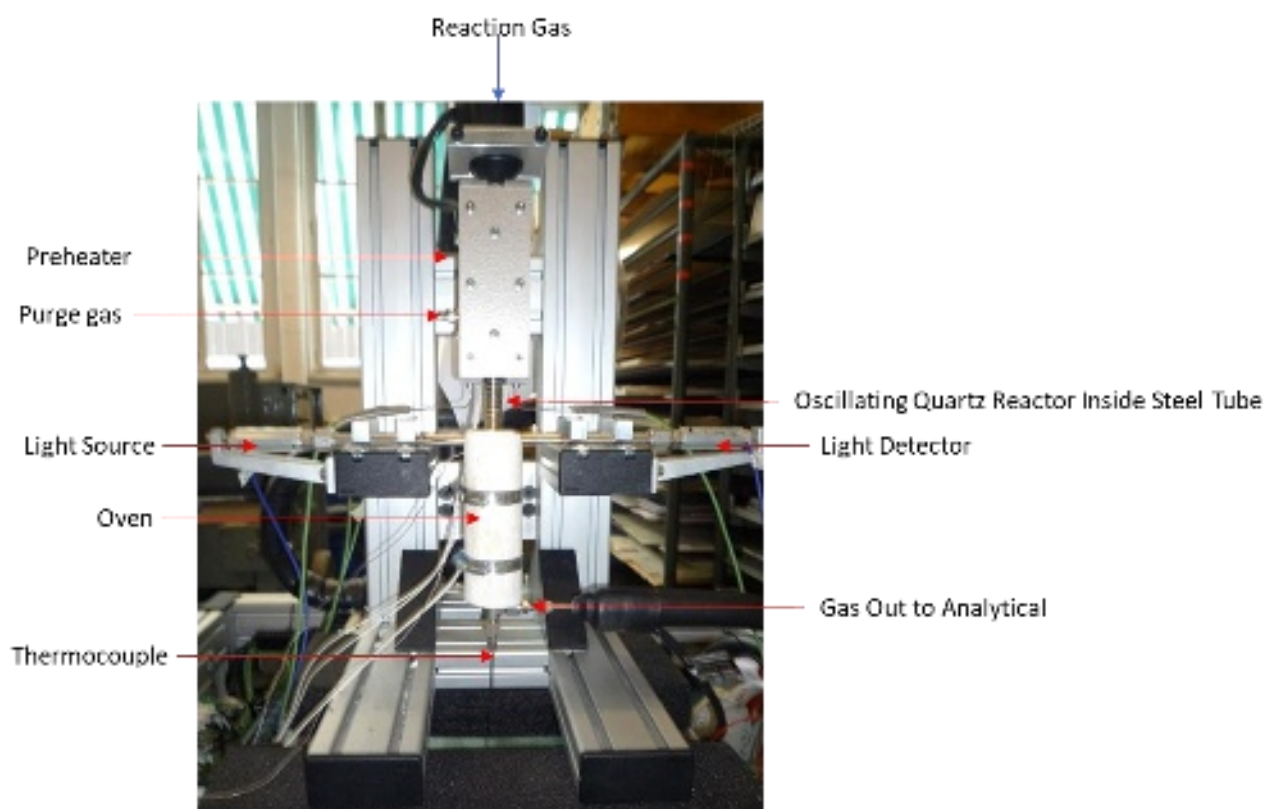


complete procedure. This includes analytical control, frequency of analysis start, GC-method to use, criteria used to move from one step to the next (normally time on step or time on oven set-point) and others. After pressing the Start Test button, the operator can leave the system unattended and return when the test is over after a day, a week, or a month. All relevant data and additional files are stored in a dedicated test-folder, with typical datafiles being ASCII based, enabling opening them in any kind of processing tools afterwards. These unattended tests can be paused during run and the remaining steps can be edited before continuing.

The tailor-made feed system typically consists of 4 or more gas mass flow controllers (GFC) and a backpressure controller (BPR), followed by a single GFC. The 4 GFC's can be set up to produce a mixture of any given ratio to be consumed by the single GFC afterwards for feeding the reactor. The BPR sets the inlet pressure to the GFC and leaks out a fixed surplus of the gas mixture. In addition, a typical feed system would also contain several other gas lines for the chemistry involved, some inert lines for dilution and purge of the system, and potentially also a liquid feed line with an evaporator. The feed and product lines in and out of the reactor, and the line to the analytical are heat traced.

The advantages of constructing the ISMA as a complete system with an advanced feed system and control of the analytical are significant.

- Exact timestamping of data and events from complete system simplifies data handling afterwards.
- Directly accessible parameters related to process, ISMA and analytical instruments.
- Full control of analytical instrument with process parameters.
- Minimize excess of analytical data.



**Figure 3.** Physical layout of the new ISMA instrument.

### User friendliness

ISMA is designed as a user friendly, robust, versatile, multi-operator instrument. It can be operated by personnel with standard laboratory skills. The main manual operation is filling of sample into the quartz element, inserting the glass element into the steel tube, and closing two Swagelok connectors. Since all parts are machined and connected using Swagelok, the quartz element is in the same position during each run, which ensures run-to-run reproducibility. All other parameters, e.g., gas compositions, flow rates, pressures, and temperatures are set in the computer software.

### Reactor and oscillating element

The user can easily switch between quartz elements with different sample volumes (Figure 4). Simply unscrew one element and replace it with the other. For the same reason, broken quartz elements can be rapidly replaced. For each element, the force constant  $k$  (Equation 1) must be determined before absolute masses can be measured, but once determined it does not have to be redetermined if the elements are replaced and later reused. Spare elements for quick and easy replacements are significantly easier and cheaper to get a hold of than what was the case for the original TEOM 1500.



**Figure 4.** Upper: Standard reactor with sample, quartz and locking-pin. Lower: Empty large reactor.

### Mass signal tuning

ISMA is designed so that only the inner quartz tube is removed when the sample is replaced. The outer, steel reactor with the fixed heaters (the main oven and the pre-heater), remains untouched in the system. Once the quartz reactor is positioned correctly inside the steel tube, the system works perfectly every time, and run-to-run reproducibility is ensured. In terms of reproducibility, operator time consumption, and reliability, this is a significant improvement from the previous TEOM 1500.

### Detector lifetime

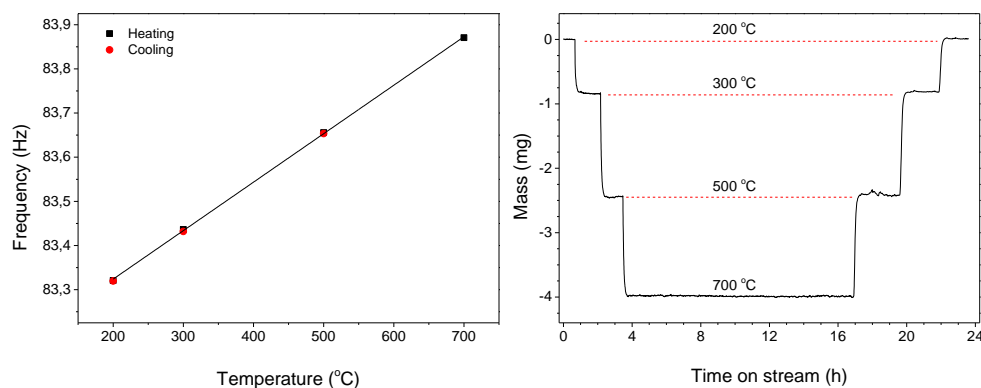
The oscillations are optically detected, and the signal is transmitted through quartz rods. We have not yet detected any deterioration of the quartz rods in the ISMA system, but if it should happen, the rods can easily be replaced. This is also an improvement compared to the extinct TEOM where the signal sending-receiving end-surfaces of the quartz rods gradually deteriorated, getting whitish, when exposed to certain atmospheres. This was particularly important with steam in the system. Steam is a common component, either used as a reactant or formed as a product, and the quartz rods had therefore to be replaced regularly.

## Heating and temperature profiles

Heat is provided to feed and product lines, the sample, and a preheater (Figure 3). The heaters are permanently mounted and there is no need for heating wires nor blankets. This ensures stable and reproducible temperature profiles in the section of the quartz tube where the oscillation takes place, and in the feed and product lines. By using heaters fixed to the set-up, and avoiding heat wires and blankets, the temperature profile variations between different runs and operators can be neglected. The ISMA heating system allows for studies up to 700 °C. No drift in the temperature profile nor in the mass signal has been detected, which is another significant improvement compared to the extinct TEOM.

### Demonstration 1: Temperature and pressure stability, and time response

Stable temperatures and pressures are required if high quality data are to be obtained. First, stable conditions are obviously required to justify claims of well-defined experimental conditions. Second, the oscillation frequency depends on the surrounding gas density and temperature, and any intrinsic temperature sensitive material properties related to quartz' behavior as an oscillator. Since the mass is calculated from the measured frequency (Equation 1), the mass signal will also respond to temperature changes. This is illustrated in Figure 5 where an empty quartz element is heated to 700 °C. The apparent mass drop with increasing temperature is due to a change in frequency from which the mass is calculated (Equation 1), and not a mass loss. Figure 5 also shows that the frequency and temperature are linearly dependent in the range 200 – 700 °C.



**Figure 5.** Left: average oscillating frequency at temperatures 200 – 700 °C. The straight line is a guide to the eye. Right: mass calculated from the measured frequency of an empty quartz element at different temperatures. The horizontal dotted lines are guides to the eye.

Figure 5 shows that the same frequency is measured during heating and cooling at each temperature, as required for a well-working instrument, and the standard deviation in the calculated mass is low. The stable temperatures are given in Table I. Furthermore, the target temperature is reached quickly, and after approximately 15 minutes ISMA is stable to within 0.01 mg. At constant pressure and temperature, the mass remains constant. This is shown in Figure 6 where the measured mass remains constant at  $171 \pm 0.04$  mg over 13 h at  $55.5 \pm 0.01$  bara and  $217.5 \pm 0.4$  °C.

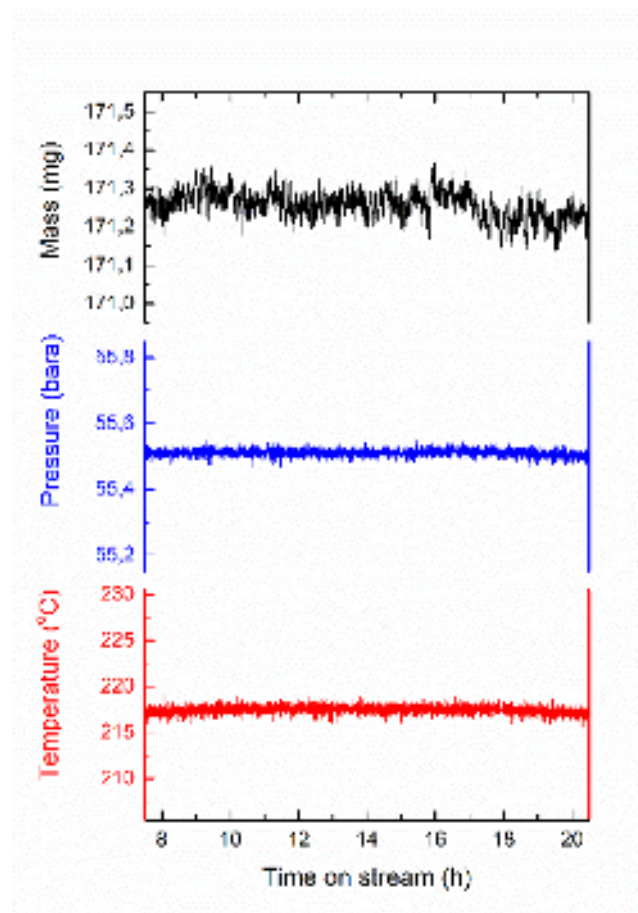


**Table I.** Apparent mass of an empty quartz element at different temperatures. The values are given as average  $\pm$  standard deviation. All masses are in mg.

	Temperature ( $^{\circ}\text{C}$ )			
	200	300	500	700
<b>Heating</b>	$0.000 \pm 0.003$	$-0.844 \pm 0.003$	$-2.439 \pm 0.003$	$-3.986 \pm 0.007$
<b>Cooling</b>	$-0.009 \pm 0.002$	$-0.812 \pm 0.004$	$-2.421 \pm 0.008$	

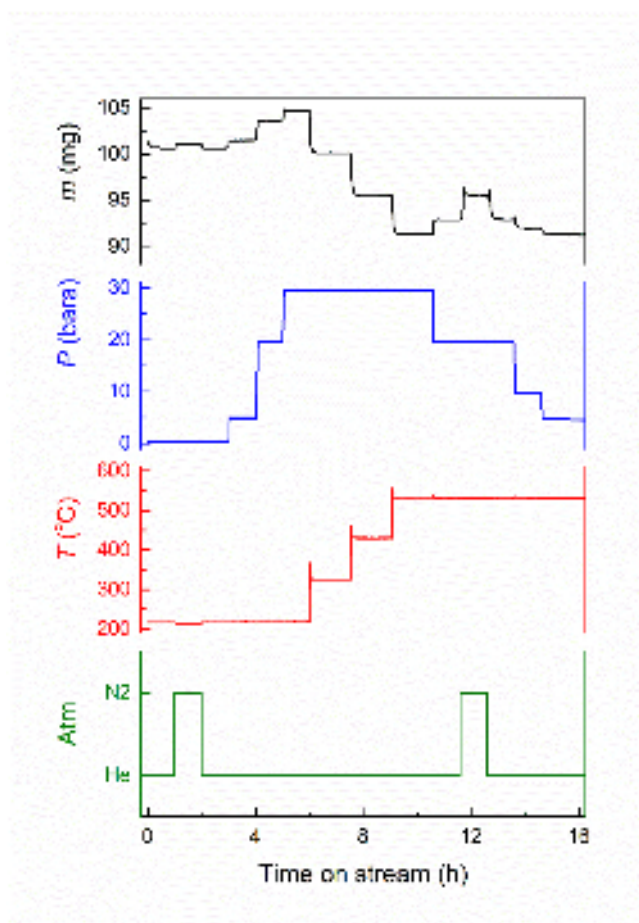
It is illustrative to compare experimentally reported values for blank runs. From Figure 2 in the paper by Chen et al.<sup>29</sup>, we estimate the max – min variation to be approximately 0.033 mg over approximately 3 minutes. For ISMA, the max – min difference to be approximately 0.014 mg over 3 minutes (Figure 5). Thus, the peak-to-peak noise level expressed as max – min variation in the ISMA signal is roughly half of the value obtained for TEOM for a blank run.

Furthermore, a mass change will instantaneously influence on the oscillation frequency. After considering signal processing parameters such as sampling rate and averaging, the time-resolution of the ISMA is approximately 0.2 s. The inherent time response of the glass element / optical system combination is an order of magnitude faster and the overall response can be tuned and shorter if required.

**Figure 6.** Mass at constant pressure and temperature. Upper (black): average mass =  $171.25 \pm 0.04$  mg; middle (blue): average pressure =  $55.51 \pm 0.01$  bara; lower (red): average temperature =  $217.5 \pm 0.4$   $^{\circ}\text{C}$ .

## Demonstration 2: Multiple steps

The ISMA core is connected to a control and feed system which enables the user to change temperatures, pressure, and feed compositions, while simultaneously *in situ* measure the mass. The system is fully automated, and control and logging are done within the same software running on one computer, so all parameters are related to the same clock. As explained above, the experimental conditions are programmed in the software method builder. When the experiment has been started, it can be left unattended. An example is shown in Figure 7, where the quartz element was charged with an inert sample and no mass was gained nor lost during the run. Thus, it exemplifies how the measured mass depends on the experimental conditions such as pressure, temperature, and atmosphere.



**Figure 7.** Multi-step experiment. From top to bottom: mass (upper black), pressure (blue), temperature (red), and atmosphere (bottom green).

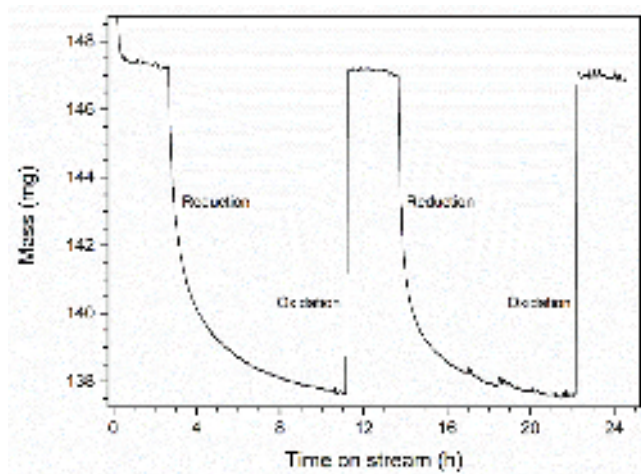
The example shown in Figure 7 consist of 13 steps over 16 h. No manual operations were required during the run as the whole sequence was pre-programmed. We have conducted runs with more than 10.000 steps running for more than five weeks. The only manual operations were to ensure that the feed reservoirs never emptied.

## Demonstration 3: Oxidation-reduction of Ni

The examples shown above were carried out in the absence of any mass changes in the sample, only frequency changes due to the reaction conditions. We will now present a study of ISMA's

applicability when a mass change in the sample occurs. The example is reduction-oxidation of NiO/Ni at 600 °C, 1 bar, and under H<sub>2</sub>- and airflow, respectively.

Figure 8 below shows the measured mass during reduction and oxidation, and in Table II we list the calculated reduction and oxidation values. As seen, they were close to 100% for all steps, slightly lower for second step than the first.



**Figure 8.** Two NiO/Ni cycles at 600 °C under reducing (H<sub>2</sub>) and oxidizing (air) conditions.

**Table II.** Experimentally measured percentage reduction and oxidation of maximum theoretical. Numbers in %.

1 <sup>st</sup> cycle		2 <sup>nd</sup> cycle	
Reduction	Oxidation	Reduction	Oxidation
100.7	99	98.4	97.2

### Experience so far and future development

Even though the new ISMA and the extinct TEOM have rather similar specifications regarding max temperature, max pressure and sample size, the complete redesign of the core components, combined with all advantages of using more modern electronics and software, has given a much more stable, robust, and user-friendly analytical instrument. The new ISMA unit has a unique capability where both reactivity and sample weight can be measured *in situ* in a plug flow system. Its capabilities and possibilities exceed the old TEOM in most respects, as documented above. Various applications can be investigated: adsorption/desorption studies, catalyst characterization, reaction kinetics, deactivation, and regeneration study due to coke, etc.

ISMA can be utilized to directly measure and improve process control parameters due to rapid feedback and high resolution of the signal. Currently SINTEF is involved in more exciting expansions of the ISMA's capabilities since customers and applications require even more challenging specifications. Plans are ready for implementing a high temperature version of ISMA that can go up to 900°C, and in the EU project eQATOR we are cooperating with the Belgian company MEAM on how to use microwaves to heat the catalyst bed.

## Conclusion

A high-performance combined fixed-bed reactor and *in situ* mass analyzer (ISMA) relevant to sub-second time resolved studies of mass changes that occur due to process conditions has been developed. The instrument is robust, user-friendly, and fully automated including built-in safety. The mass is calculated from the optically measured oscillation frequency of a quartz element, yielding microgram mass resolution for samples up to 500 mg. The instrument is applicable up to approximately 62 bar and 700 °C. When ISMA is combined with a suitable feed system and product analysis set-up, time resolved studies are enabled.

## Acknowledgments

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## Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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## Figure captions

**Figure 1.** ISMA sketch. Heaters omitted for clarity. Not drawn to scale.

**Figure 2.** Measured amplitude (orange) and phase (grey). Upper: Intermediate results. Lower: Final result with an element oscillating in its fundamental mode at 48 Hz. At 64 Hz we find the transverse mode of the element. The transverse mode is visible because it is difficult to align the element 100%.

**Figure 3.** Physical layout of the new ISMA instrument.

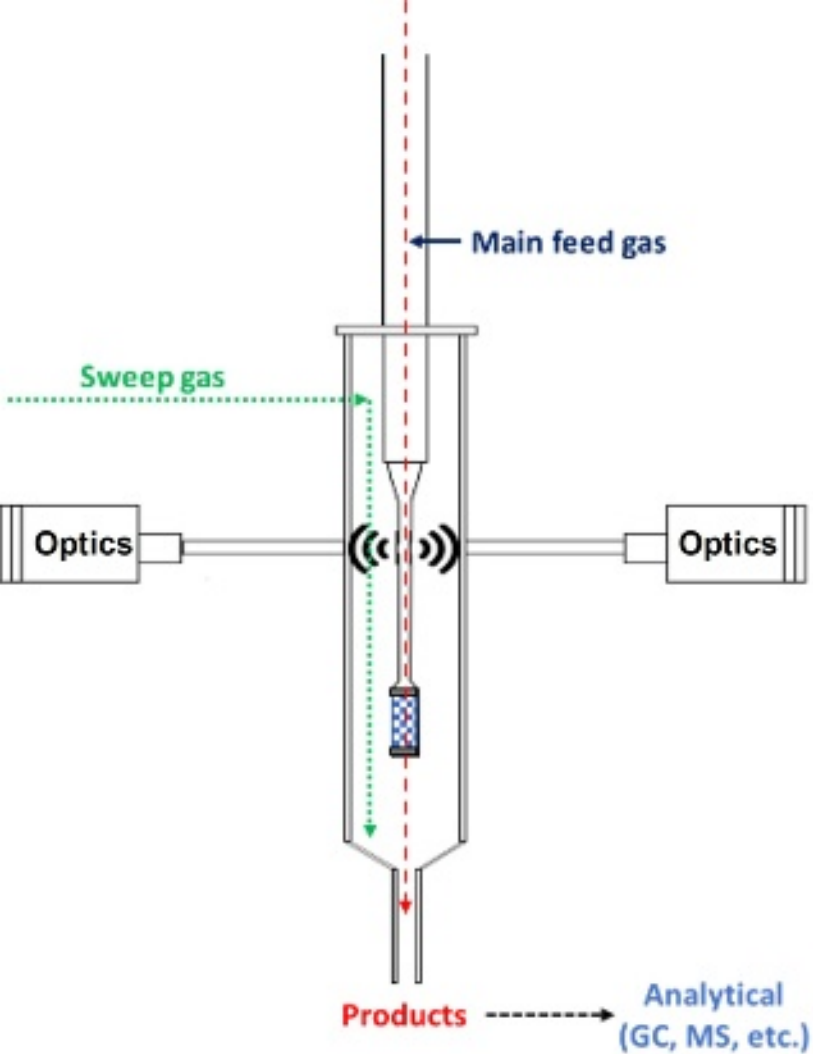
**Figure 4.** Upper: Standard reactor with sample, quartz and locking-pin. Lower: Empty large reactor.

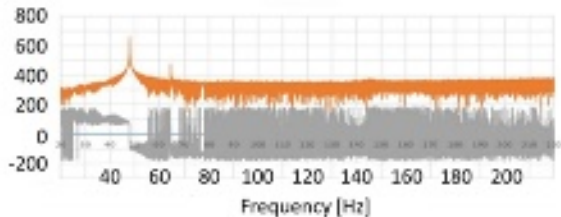
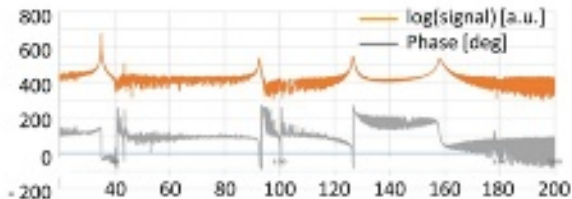
**Figure 5.** Left: Average oscillating frequency at temperatures 200 – 700 °C. The straight line is a guide to the eye. Right: Mass calculated from the measured frequency of an empty quartz element at different temperatures. The horizontal dotted lines are guides to the eye.

**Figure 6.** Mass at constant pressure and temperature. Upper (black): average mass =  $171.25 \pm 0.04$  mg; middle (blue): average pressure =  $55.51 \pm 0.01$  bara; lower (red): average temperature =  $217.5 \pm 0.4$  °C.

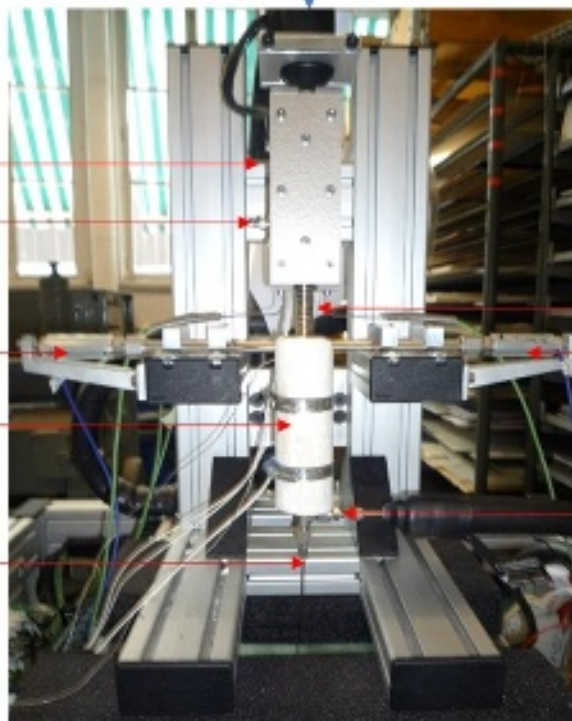
**Figure 7.** Multi-step experiment. From top to bottom: mass (upper black), pressure (blue), temperature (red), and atmosphere (bottom green).

**Figure 8.** Two NiO/Ni cycles at 600 °C under reducing (H<sub>2</sub>) and oxidizing (air) conditions.





Reaction Gas



Preheater

Purge gas

Light Source

Oven

Thermocouple

Oscillating Quartz Reactor Inside Steel Tube

Light Detector

Gas Out to Analytical

