TP 15432E

Effectiveness of Mercury Spill Remediation Techniques

Project Report

Prepared for:

Transport Canada

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Prepared by:

Parole Laboratories Inc.

1150 Dumont Avenue,

Dorval, QC H9S5W1

info@po-labs.com

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Finally, I wish to thank my family and friends for their support and encouragement throughout this project.

Oleg Nepotchatykh, Ph.D.

List of Abbreviations

CANUTEC – the Canadian Transport Emergency Centre

Rpm (rpm) – revolutions per minute

CVAFS – Cold Vapour Atomic Fluorescence Spectroscopy

EPA – United States Environmental Protection Agency

AAS – Atomic Absorption Spectroscopy

g – Unit of weight, grams

g – The gravity of Earth, centrifuge acceleration unit; is equal to 9.78 m/s^2

λ – Wavelength

nm – nanometre, equal to one billionth of a metre

μL – microlitre, 1/1000,000 of litre

mL – millilitre, 1/1000 of litre

ACGIH – The American Conference of Governmental Industrial Hygienists

ORP – Oxidation Reduction Potential

Definitions

Conversion efficiency: Percentage of initial amount of mercury, transformed into mercuric sulphide or mercuric acetate to a certain time point.

Yield of a reaction: Equal to the mercury conversion efficiency.

Standard ambient conditions: Temperature 20°C and atmospheric pressure (101,325 Pascal).

A double-beam instrument: A spectrometer with analytical cell and reference cell illuminated by the same source, resulting in lower interferences and noise compared with single-beam instrument.

Teflon®: Polytetrafluoroethylene.

LabVIEW®: A graphical programming language, developed by National Instruments Co. for instrument control and data acquisition.

Thermistor: An electronic sensor designed for temperature measurement. Typically it increases resistance with temperature.

Pyrex®: A sort of laboratory glass with high chemical resistance and high melting point.

Standard molar enthalpy: Energy released or consumed at formation or decomposition of one mole of a compound.

Standard oxidation-reduction potential (E^o): An electrical potential in Volts produced by electrochemical reaction at standard conditions and measured against standard hydrogen electrode.

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Introduction

Mercury is a metal with many important properties, and therefore it has been known and used since ancient times. Mercury, despite its extreme toxicity [1], is still essential for many industrial applications and devices. As a result, many household devices contain mercury, such as thermometers, thermostats, fluorescent lamps, some blood pressure monitors, barometers and others. Typically, elemental mercury is sealed into a glass enclosure, ampule or a tube to avoid evaporation. Such a device, containing metallic mercury, could be accidentally broken and a mercury spill could occur. Taking into account the extreme toxicity of mercury and its volatility [2], proper actions are required to clean up the spill and prevent toxic effects on humans. The Canadian Transport Emergency Centre (CANUTEC) suggested cleaning mercury spills by physical recuperation of large mercury drops and then wiping the spill area with vinegar followed by hydrogen peroxide. CANUTEC has also previously recommended the use of sulphur powder to convert small mercury droplets to inert mercuric sulphide. Although these two methods of mercury remediation and spill site decontamination have been commonly used for some time, their effectiveness is unknown. In particular, the mercury conversion efficiencies into mercuric acetate and mercuric sulphide in those two methods are unknown, and it is unclear how, or if, these two methods prevent further emissions of mercury vapours. Moreover, the influence of mixing mercury with the previously mentioned reactants in relation to the conversion efficiency is unknown as well. The present project was dedicated to answering some of these questions.

Objectives

The main objectives of this project were to measure conversion efficiency of mercury into mercuric sulphide (Task 2) and mercuric acetate (Task 3) while measuring the mercury evaporation into the air (Tasks 1 – 3), accompanied with temperature and pressure measurements.

Task 1 – Production of Mercury Vapours from Nascent Metallic Mercury

The goal of Task 1 was to test the propensity of elemental mercury to produce vapours under standard ambient conditions in a closed vessel over a period of 120 hours. During this period, the concentration of mercury vapours in the container was measured using two suitable independent analytical methods. The experiments were conducted with undisturbed mercury and repeated with mixing at 150 rpm.

Task 2 – Conversion Efficiency of Metallic Mercury to Mercuric Sulphide Using Sulphur Powder

The goals of Task 2 were to test the efficiency of the conversion of elemental mercury into mercuric sulphide when it was combined with an excess of sulphur powder, and to estimate the associated mitigation of the release of mercury vapours, as well as to monitor the temperature and pressure in the reaction vessel. The experiments were conducted over a period of 120 hours with undisturbed mercury, and repeated with mixing at 150 rpm.

Task 3 – Conversion Efficiency of Metallic Mercury to Mercuric Acetate Using Vinegar and Vinegar-Hydrogen Peroxide Mixture

The goals of Task 3 were to test the efficiency of the conversion of elemental mercury into mercuric acetate in a reaction with vinegar over a period of 60 minutes, and then adding hydrogen peroxide to test the mitigating power of the vinegar – hydrogen peroxide mixture for an additional 60 minutes, estimate associated mitigation of the release of mercury vapours, and monitor the temperature and pressure in reaction vessel. The experiments were conducted with undisturbed mercury and repeated with mixing at 150 rpm.

Materials and Methods

Warning: Elemental mercury in form of liquid, mercury vapours, and all mercury compounds used, or produced, in this project are extremely toxic and could be fatal in small quantities. A person, who intends to handle mercury and its compounds must have appropriate training, protection, and equipment.

Materials

In this project the following materials were used: Metallic mercury, 99.99%, Sulphur, 99.9%, and Mercuric Acetate, 99.5%, purchased from A&C American Chemicals Inc., Montréal, Québec; sulphur powder “Garden Sulphur” made by GreenEarth®, purchased from Canadian Tire, St-Laurent, Québec; No Name® vinegar (5% Acetic acid), purchased from Maxi grocery store, Dorval, Québec; Hydrogen Peroxide Life Brand® (5% W/V), purchased from Pharmaprix, Dorval, Québec; Dimethylformamide of HPLC grade, Dichlorodimethylsilane, 2% solution in toluene, Sodium Dodecyl Sulphate 99.5%, Diphenylcarbazone, and Diphenylcarbazide purchased from Sigma-Aldrich® Oakville, Ontario.

Methods

Analytical methods used to measure the concentration of mercury vapour in the air for all three tasks were:

Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS)

The first analytical method used in this project was Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS) [3]. A sample of air from the flask (100 µL) was periodically injected into a Tekran® 2600 CVAFS spectrometer for analysis (Figure 1). The settings of the instrument were the same as for EPA method 1631 [4]. The instrument was initially calibrated with a Tekran® Model 2505 Mercury Vapour Calibration Unit according to the manufacturer’s and EPA standard procedures [5, 6].

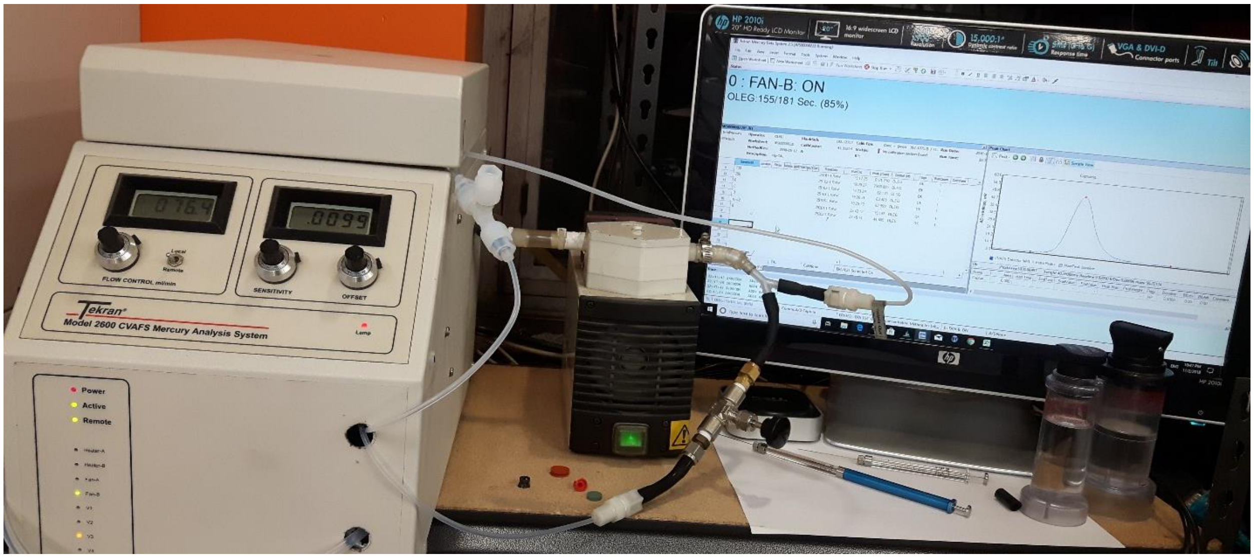

Figure 1. A photograph of the Tekran® 2600 CVAFS spectrometer.

Atomic Absorption Spectroscopy (AAS)

The second method of analysis of mercury vapour concentration was specially developed for this project and was based on Atomic Absorption Spectroscopy (AAS) [7]. We modified the Coleman® Model 50B AAS spectrometer (Figure 2) to make it a double-beam instrument with the addition of acid and ozone traps.

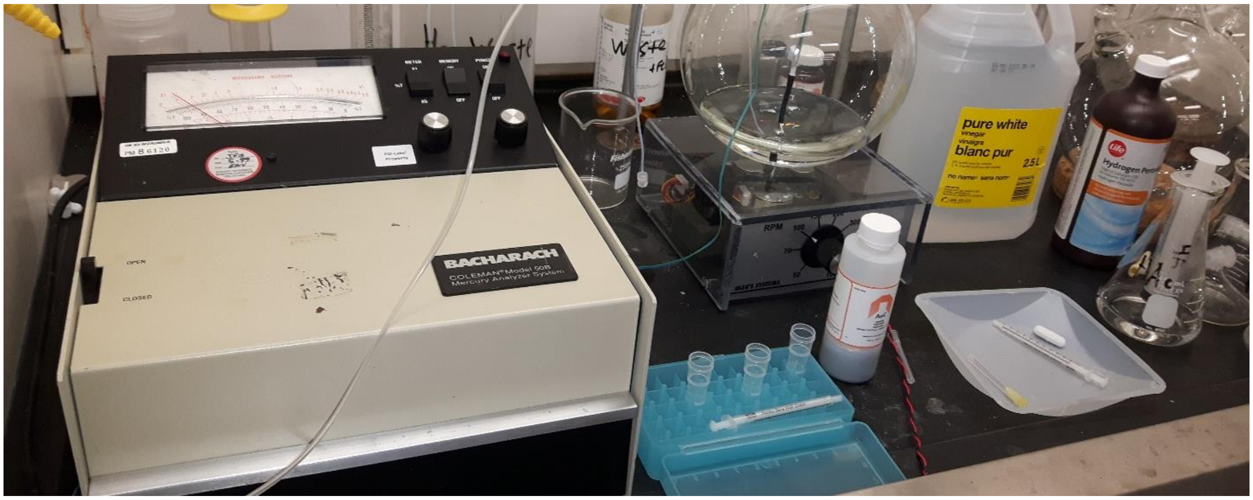

Figure 2. A photograph of the modified Coleman® Model 50B AAS spectrometer.

A small diaphragm pump was included to integrate this AAS instrument into the experimental setup for continuous real-time measurement of mercury vapours. The pump transferred the air from the reaction flask into the analytical cell of the AAS spectrometer trough two Teflon capillaries, installed into the left sampling port of the reaction flask (as shown in Figure 5), and returned the air to the reaction flask, resulting in a closed circulation loop. The signals from two spectrometer's UV photodiodes (detectors) were amplified and transferred to a computer using appropriate electronics and Ontrak® ADU100 USB data acquisition interface [8] (as sown in Figure 3).

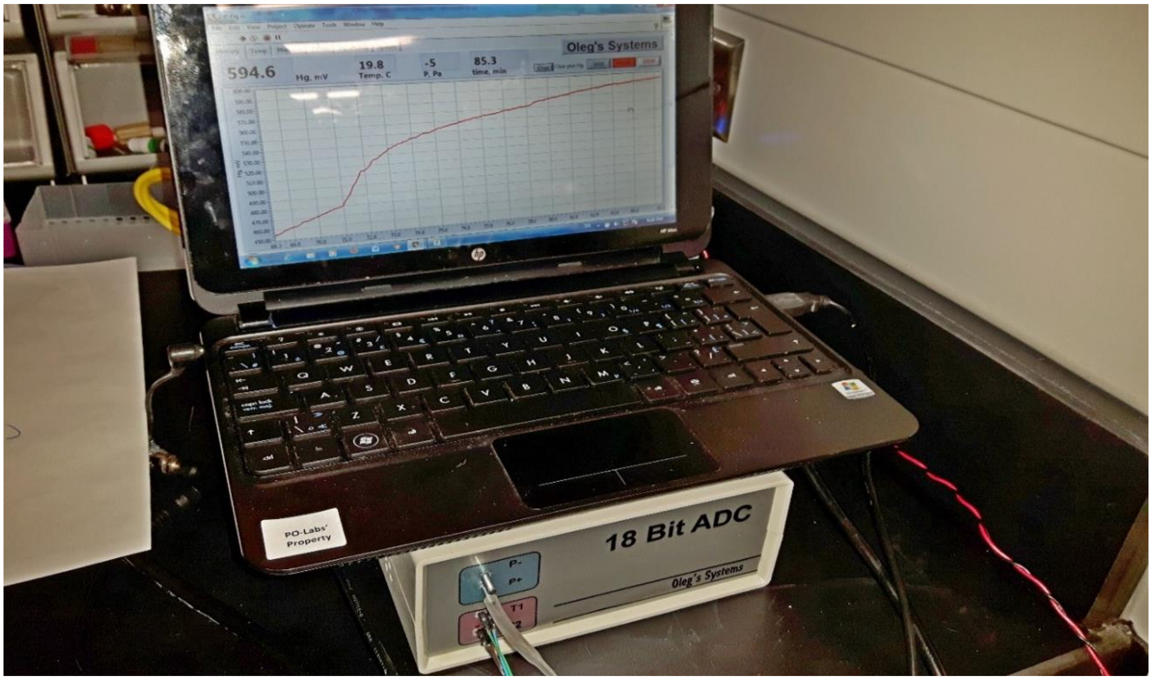

Figure 3. A photograph of Ontrak® ADU100 USB data acquisition interface connected to the AAS spectrometer, pressure sensor, temperature sensor and other electronics in a shared enclosure and a computer running LabVIEW® Virtual Instrument on top of it.

We engineered a software (a LabVIEW® virtual instrument) to control the instrument automatically; this was required for the development of a real-time continuous analytical method. We used one sample per second as the data acquisition rate; however, the acquisition rate could be adjusted over a broad range. The original needle indicator on the front panel of the Coleman® Model 50B AAS spectrometer remained in place; however, it was not used for data acquisition, because the computer fully controlled the instrument. The AAS method was calibrated using standardized mixtures of purified air with mercury that was prepared by precise dilution of saturated mercury vapour with known concentration. Compared to CVAFS, AAS showed similar sensitivity and very close results in the analysis of standard samples, quality control, (as in Figure 4) and actual experimental samples.

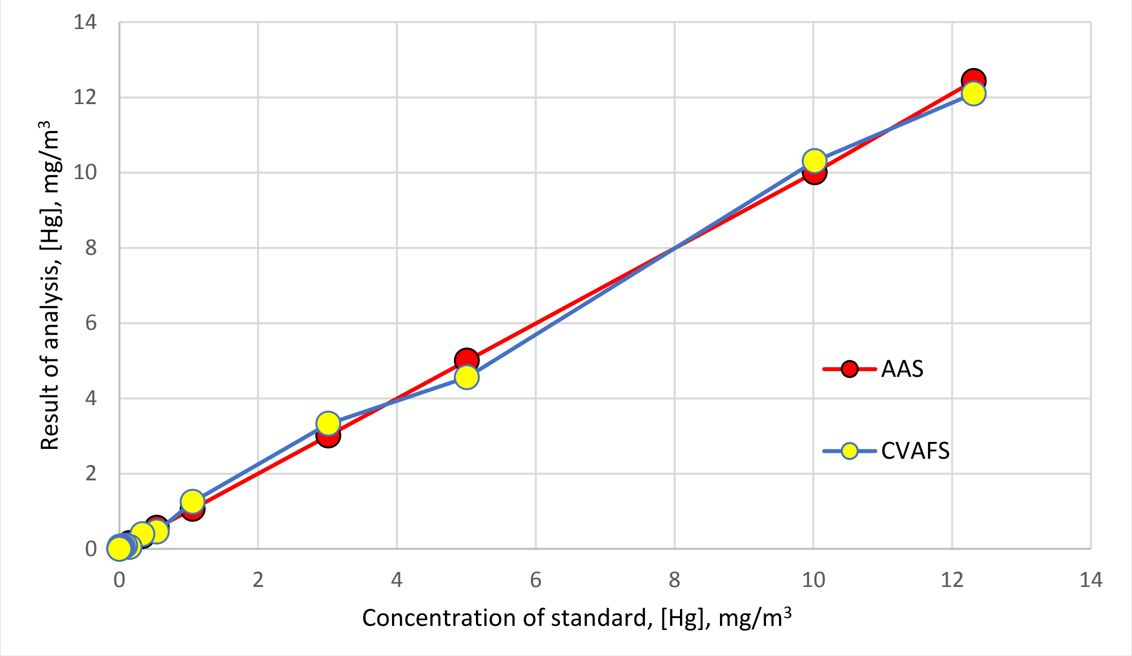

Figure 4. Results of analysis of standard samples of mercury vapours by the AAS and CVAFS methods.

A substantial difference, however, is that AAS is a continuous non-destructive method, while CVAFS is destructive and requires periodic sample collection using a gas-tight syringe once per three minutes at the fastest rate. As a result, the CVAFS method produced fewer data points compared with AAS.

Temperature and pressure measurement

In all experiments, temperature and pressure inside of the reaction flask were recorded using GE Nova® 1210 solid-state pressure sensor [9] and Omega® 44005 precision thermistor [10], sealed into a Teflon-glass probe. Both sensors were connected to the computer via Ontrak® ADU100 USB data acquisition interface shown in Figure 3. The temperature sensor was calibrated using melting points of pure water, acetonitrile and camphor. The pressure sensor was calibrated against a water column manometer.

Reaction vessel

As a vessel for mercury experiments, a 3-litre round reaction flask (Figure 5) made of Pyrex® with appropriate ports for sampling and insertion of a temperature probe was used. The reaction flask was treated from the inside by silanization reagent (solution of dichlorodimethylsilane) to passivate it and prevent mercury adsorption on the glass surface.

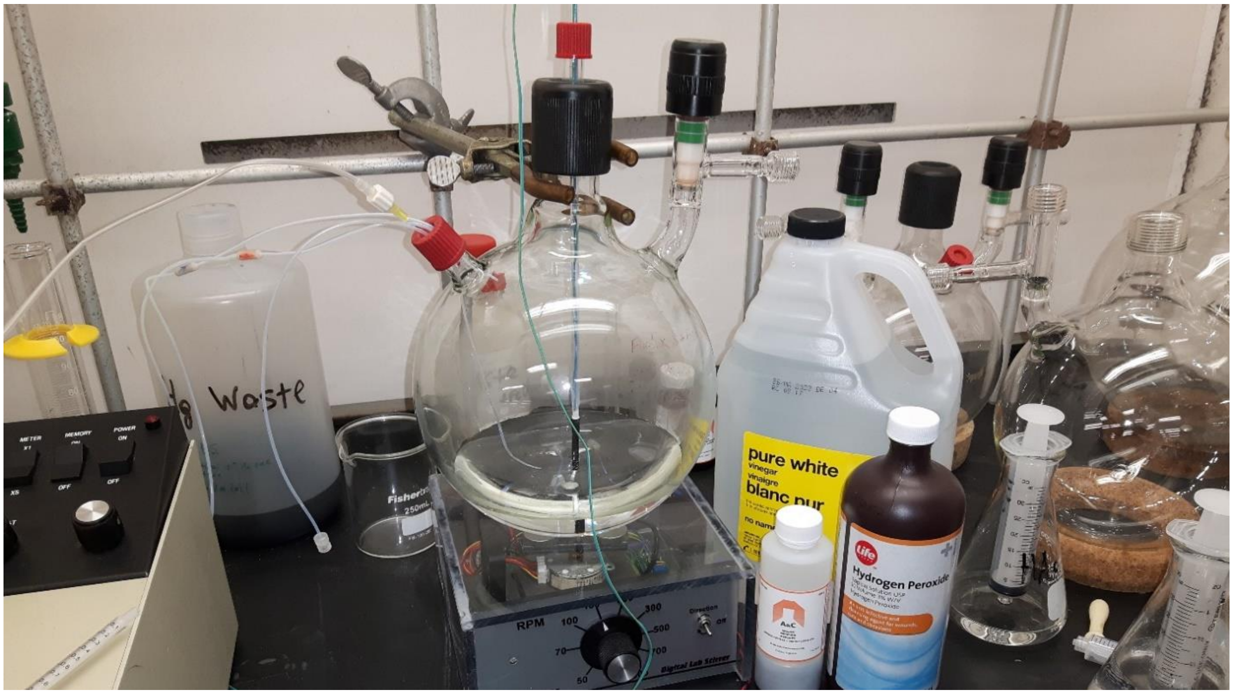

Figure 5. A photograph of the 3-litre round reaction flask. The temperature probe inserted from the top. The AAS spectrometer connected with the flask using two Teflon capillaries (outlet and inlet) inserted through the septum on the left side. The same port also connected with the pressure sensor and had a capillary with a Luer adapter. The capillary with the Luer adapter extended to the bottom of the flask and allowed mercury injection and collection of liquid samples from the flask. The port on the right allowed venting the flask and flushing it with purified air before each experiment.

Experiments with mercury vapours in a reactor made of Teflon® were attempted initially (Figure 6); however, we discovered that Teflon® was permeable to mercury vapours. The type of Teflon® material used for manufacturing of this reactor was made by powder compression technology which resulted in micro-porous structure. Teflon has also been used as part of several other instruments and parts such as probes, magnetic stirring bars, capillary tubes, and temperature sensor coating within this project; however, in these cases Teflon was manufactured by hot melt extrusion technology and did not have such a problem. Consequently, all experiments within this project were conducted in a Pyrex reactor with internal silanization instead.

Figure 6. Two photographs of a reactor made of Teflon®.

Digital stirrer

All experiments were conducted with undisturbed mercury and repeated with mixing at 150 rpm to investigate the effect of mixing on the mercury conversion efficiency and evaporation rate as previously agreed. Ordinary laboratory magnetic stirrers usually have speed control knobs; however, they may not maintain or be pre-set to specific rotation speed. In this project, a homemade digital magnetic stirrer, which was specially designed to maintain a specified rotation speed of magnetic field independently of a load or mixed liquid viscosity, was used (Figure 7). The stirrer was calibrated against a quartz frequency counter.

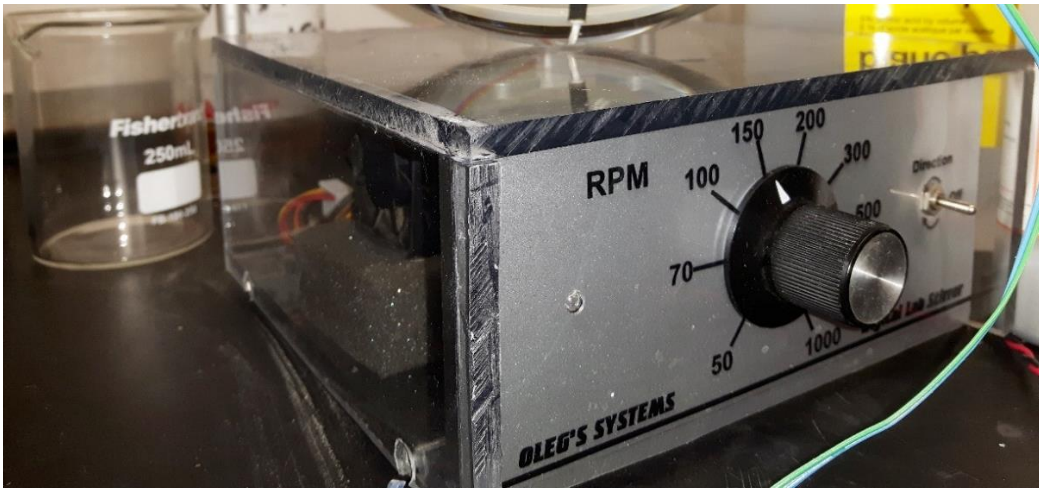

Figure 7. A photograph of the digital magnetic stirrer.

Methods used for Task 1:

Methods used for Task 1 were CVAFS and AAS.

Procedure for Task 1 experiments:

For an experiment, a portion of mercury (refer to Addendum raw data), weighted to 0.1 mg was transferred to the bottom of the reaction flask as one single drop using a 1 mL plastic disposable syringe, connected to a Teflon capillary with a Luer adapter. The precise amount of mercury (weighted to 0.1 mg) used in an experiment was determined by the weight difference of the syringe before and after mercury injection. The Luer adapter was modified to allow injection of mercury without residual drops in it and in the capillary. Some mercury drops, however, remained in the syringe, but that was accounted by weight. At the time of mercury injection into the reaction flask, data acquisition of AAS instrument was initiated. The air samples were periodically taken from the sampling port of the reaction flask and analyzed by CVAFS instrument. Experiments were conducted at ambient temperature and pressure for 120 hours. For the second part of Task 1, mercury was mixed at 150 rpm with a magnetic stirring bar, coated with Teflon®. Experiments were repeated in duplicate.

Methods used to measure the conversion efficiency of mercury for Task 2:

Conversion efficiency of mercury to mercuric sulphide was measured using two methods:

Spectrophotometric method of sulphur analysis

The first method was based on a spectrophotometric determination of remaining sulphur content. This method we developed using sulphur's spectral and solubility information published by Tomio Okada [11]. The reaction mixture containing mercury, sulphur, and mercuric sulphide was treated with exactly 100 mL of toluene using GE-50 ultrasonic processor, then the suspension was centrifuged at 5000 *g*. After that, about 3 mL of the liquid phase was placed into a Pharmacia® LKB Novaspec II spectrophotometer operated at λ=370 nm for direct analysis of sulphur concentration (Figure 8). At λ=370 nm, the method was linear from 0.02 to 100% calculated from the initial sulphur amount. Amount of sulphur, consumed at a sampling time point was calculated by subtraction of the remaining amount of sulphur from the initial one. Reaction yield was calculated based on the initial amount of mercury and the amount of sulphur, consumed at the sampling time point.

The solid phase remaining after centrifugation was analyzed by the gravimetric method (I) as described below.

Figure 8. Spectrophotometer Pharmacia® LKB Novaspec II is on the left side of the photograph; analytical balances are on the right.

Gravimetric method (I) of mercury analysis

The second method used for this task was gravimetric. The principles of gravimetric methods are described in the book of Skoog D. A. et al. "Fundamentals of Analytical Chemistry" [12]. The solid phase, remaining after the previous method, was washed with acetone to remove any toluene contamination and then suspended in water containing 0.01% sodium dodecyl sulphate. Next, mercuric sulphide was separated by flotation technique [13]. The hydrophobic particles of mercuric sulphide attached to the air bubbles, which rose to the surface forming a froth, were discarded to the mercury waste. The metallic mercury remained on the bottom, and was then collected and measured by weight using analytical balances (visibly shown on the right of Figure 8). Was expected that during flotation some elemental mercury could possibly escape with HgS and we did investigate this matter during the method development. In experiments with no mixing, however, there was no such a problem, because all mercury remained as a single drop and it has been completely recovered. Mixing mercury with sulphur created a lot of small droplets. We noticed that during the sulphur dissolution stage the ultrasound treatment promoted small droplets of mercury to stick together and sink down as large drops. We also placed HgS obtained by flotation in a flask and heated it to about 130 C. There we detected only traces of elemental mercury evaporation. Besides, mass balance with sulphur showed about the same recovery of mercury, see Figures 17 and 18. The mercury recovery was estimated as better than 97%.

Procedure for Task 2 experiments:

For an experiment, the flask was flushed with purified air for several minutes to remove traces of mercury vapours, that could be present in the laboratory air, then a precisely weighed amount of sulphur (3 times molar excess to the amount of mercury) was placed into the reaction vessel. The precisely weighed amount of mercury was then injected into the bottom of the reaction flask (under the sulphur layer) as one single drop by a 1 mL plastic disposable syringe, connected to a Teflon® capillary with a Luer adapter (Figure 5). At the time of mercury injection into the reaction flask, data acquisition via the AAS instrument was initiated. Also, air samples were periodically taken from the sampling port of the reaction flask and analyzed using the CVAFS instrument.

The reaction was terminated every 24 hours (i.e. 24 hr., 48 hr., 72 hr., 96 hr., and 120 hr.) for analysis of remaining sulphur and mercury as described above. For each sampling timepoint remaining reactants were analyzed, and the conversion efficiency of mercury to mercuric sulphide was calculated. For experiments with mixing, a magnetic stiring bar coated with Teflon® was placed into the reaction vessel, and during the experiment, it was rotated at exactly 150 rpm to mix the reaction components.

Methods used to measure the conversion efficiency of mercury for Task 3:

Diphenylcarbazide spectrophotometric method of mercuric ion analysis

During the reaction of mercury with vinegar (acetic acid), or with vinegar mixed with hydrogen peroxide, the formation of mercuric acetate as a reaction product was expected. Mercuric acetate is a salt, and in the presence of water or other polar solvents, it dissociates to acetate (CH_3COO^-) and mercury (II) ions (Hg^{+2}). Hg^{+2} ions reacted with a mixture of diphenylcarbazone and diphenylcarbazide [14], which was used for mercuric ion analysis.

We developed the following procedure: A sample, containing mercuric acetate was diluted with dimethylformamide in 1:10 ratio, then 100 µL of diluted sample was added to 3 mL of diphenylcarbazone and diphenylcarbazide dissolved in dimethylformamide. The blue-coloured product with λ_{max} = 560 nm (Figure 9) was analyzed spectrophotometrically using a Pharmacia® LKB Novaspec II instrument (Figure 8). Hydrogen peroxide and acetic acid did not interfere with Hg^{+2} analysis. The method was very sensitive and linear in a broad concentration range, see Figure 40 in Appendix.

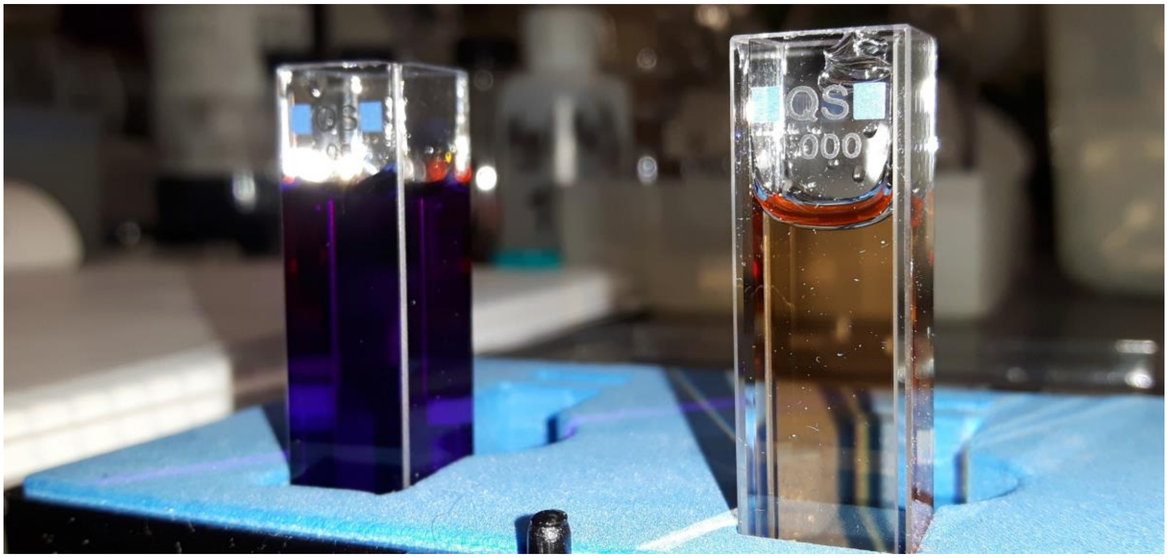

Figure 9. Spectrophotometric analysis of mercuric acetate using diphenylcarbazone - diphenylcarbazide solution. Cuvette on the left: mercuric acetate added; cuvette on the right: no mercuric acetate added.

Gravimetric Method (II) of elemental mercury analysis

The second method was gravimetric. Compared with the gravimetric method (I)~~,~~ used in Task 2, this method required no reaction termination. At each testing time point, the metallic mercury was collected from the reactor using the Teflon® capillary with an attached syringe, placed in a plastic container, measured by weight (Figure 10) and returned into the reactor in less than a minute. The procedure allowed accurate removal and return of mercury. Mercury was aspirated from the bottom of the reactor together with a portion of surrounding liquid (vinegar or vinegar+H2O2) using a capillary connected to a syringe. Part of that liquid (100µL) was analyzed for mercuric acetate and the rest was kept. Mercury was dropped from the syringe on a folded piece of filtering paper, this dried the mercury drop in an instance. Mercury does not wet paper and water. Then mercury was transferred into a plastic container and weighted (Figure 10). The remained portion of liquid, initially aspirated from the reactor, was added to mercury and together they were aspirated by the syringe. Next, the syringe was connected to the capillary and then mercury and liquid were injected back into the reactor. To do so one has to hold the syringe vertically (needle end down), so the mercury layer (heavier) enters the capillary first and then the liquid layer (lighter) follows. Flow of liquid, followed mercury, washed all mercury off the syringe and the capillary. This way was no mercury loss.

Figure 10. Gravimetric analysis. Mercury removed from the reactor is precisely weighted in a plastic container.

Procedure for Task 3 experiments:

The clean 3L reaction flask was initially flushed with purified air and then charged with exactly 250 mL of vinegar. Next, a portion of mercury (refer to Addendum raw data), weighted to 0.1 mg was injected under the vinegar layer using Teflon® capillary to avoid contact of mercury with the air in the reactor, as shown in Figure 5. Initially, there were no mercury vapours in the reactor. The reactor was then closed and all sensors and the AAS spectrometer were initiated. Small samples (100 µL) of the vinegar layer were taken from the reactor using Teflon capillary at sampling time points of 5, 10, 30, and 60 minutes. The samples were analyzed immediately for the quantity of mercuric acetate as described above. At the same time points, mercury was removed from the reactor using same Teflon capillary, precisely weighed and then returned into the reactor as described above (in Gravimetric Method (II) of elemental mercury analysis). At the 60-min time point, precisely 120 mL of hydrogen peroxide was added into the reactor. Samples of liquid mixture were taken from the reactor using Teflon® capillary at sampling time points 65, 70, 90, and 120 minutes and analyzed for mercuric acetate concentration. At the same time points, mercury was removed from the reactor using Teflon capillary, precisely weighed and then returned into the reactor to continue the experiment.

In the second part of Task 3, the same experiments were repeated with mixing of reagents by a Teflon-coated stirring bar driven by in-house made digital stirrer operated at 150 rpm.

Results and discussions

Task 1 – Production of Mercury Vapours from Nascent Metallic Mercury

Experiments on undisturbed mercury vaporization tendency were conducted in two replicates using two analytical techniques (CVAFS and AAS). The total experiment time was 120 hours (7200 min) as required by Statement of Work. The Statement of Work also required that mercury vapour concentration in the reaction vessel be measured once every 24 hours. Instead, as was previously agreed, greater number of measurements of mercury concentration (especially at the beginning of each experiment) were made using the CVAFS method. The CVAFS method did not require termination of reaction, it required periodic manual injection of a small air sample (250 µL) into the instrument. Removal of such a small volume from 3-lire flask did not create measurable change of pressure in it. As was agreed with Transport Canada experts, initial periods of experiments expected to be the most interesting and important. According to the agreement, CVAFS measurements were performed with different frequency, more frequently at the beginning and less frequent at the end of each experiment. In the other words frequency of CVAFS measurements was data dependent. This resulted in much more detailed investigation of mercury evaporation than it was intended in by Scope of Works. For the same reason we developed a continuous method. Continuous mercury vapour measurement was performed using the AAS method (one measurement per second for the entire test period). These combined measurement techniques allowed investigation of mercury evaporation with a high accuracy and detail. The results of the four experimental runs are presented in Figure 11 below.

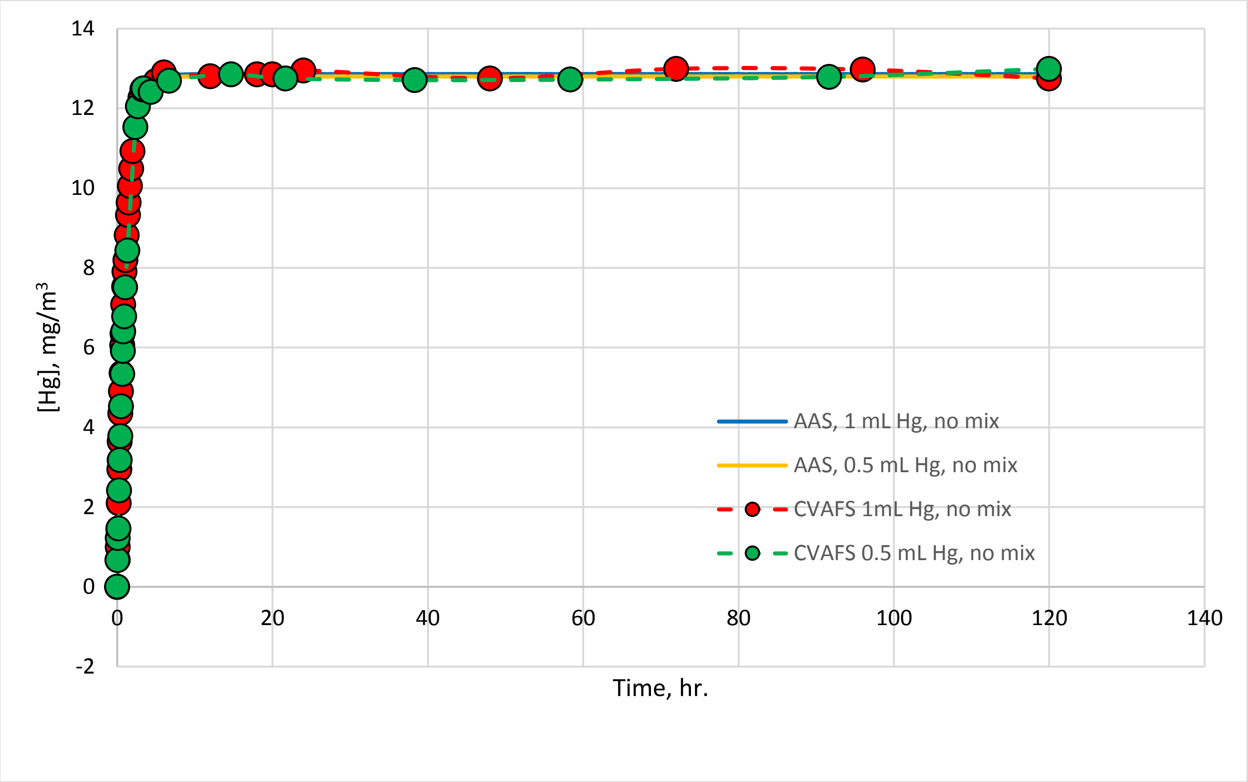

Figure 11. Change of mercury vapour concentration in air vs time produced by undisturbed mercury in closed 3 L reaction flask measured by CVAFS and AAS methods, 20°C.

The results obtained by both methods, CVAFS and AAS, were in excellent agreement with each other. As one can see from Figure 11, mercury saturated the air in the reaction flask at approximately the 500 min time point (~8 hr.), and then the concentration of mercury vapour remained constant. In terms of project objectives, the initial period of the mercury evaporation curve was the most important.

In Figure 12, data from the same experiment as in Figure 11, but for the period of the first 180 minutes, is presented. Blue and yellow lines represent continuous AAS measurement results, and red and green dots are individual test results of CVAFS method.

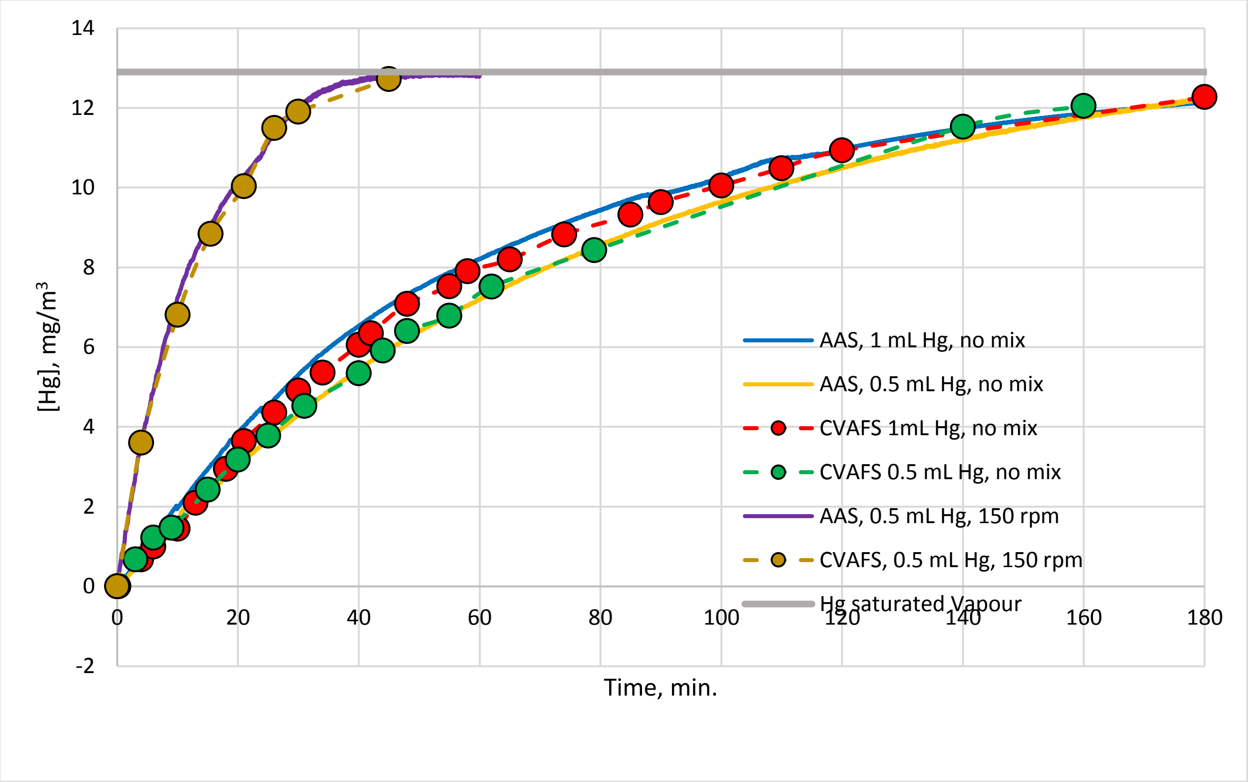

Figure 12. Change of mercury vapour concentration in air vs time produced by undisturbed or mixed mercury in closed 3 L reaction flask measured by CVAFS and AAS methods during the 180 min period 20°C.

As follows from the plot legend of Figure 12, the blue line and red dots represent evaporation from 1 mL of mercury, the green dots and yellow line represent evaporation from 0.5 mL of mercury. The results show that the evaporation rate of mercury weakly depended on the quantity of liquid mercury. The mentioned four curves were the results of evaporation of undisturbed mercury with no airflow in the reaction flask. For comparison, we performed an additional experiment where 0.5 mL of mercury was mixed at 150 rpm, and the resulted vapours were similarly analyzed during the experiment. The results of the experiment with mercury mixing are shown in Figure 12 as a purple line (AAS) and yellow dots (CVAFS). Mixing had a strong influence on mercury evaporation rate. With mixing, the mercury concentration in the air reached a saturation level (~12.9 mg/m^3) in approximately 40 minutes. Compared with the undisturbed mercury experiment, this was about ten times faster.

Rotation of stirring bar divided mercury into a few smaller droplets and created a weak air movement inside of the reaction flask. In case of an accidental mercury spill, such as breaking a thermometer, most likely spilled mercury will form small droplets and together with an air movement in that room, a dangerous concentration of mercury vapours will quickly fill the room.

Obtained results could be interpreted in the following way: mercury saturates the air in the near proximity relatively fast, but as soon as air gets saturated, the mercury evaporation stops, as for any other liquid. If there is no air movement mercury vapour diffusion is due to molecular mobility, which takes time, like 3-4 hours for 3-litre volume (figure 12). In the case of mixing, the surface of mercury increases, because it forms smaller drops. The larger surface should increase the evaporation rate. However, as a more important factor could be considered the air movement across the mercury surface, which was created by a rotating stirring bar. Both factors (small drops and air movement) applicable to household mercury spills, because there is always some air movement in any room, even without mechanical ventilation. Some parts of a room or objects may have a different temperature, and that is enough to create air movement. Mercury is a heavy element; however, the saturated mercury vapour has a very small concentration of 13 mg/m^3. Accordingly, the mercury vapour has virtually the same density as the clean air (at the same temperature), and as a result, mercury vapour will not form a gas layer close to the ground as it could be observed for heavy gases, like chlorine. All those factors (evaporation rate, air movement and low density of vapours) could result in a rapid rise of mercury concentration in a room in case of a mercury spill. To estimate such a period, it is essential to look at the change of mercury vapour concentration during a few first minutes of the experiment. In Figure 13 presented the rise of mercury concentration in the air within the first 5 minutes.

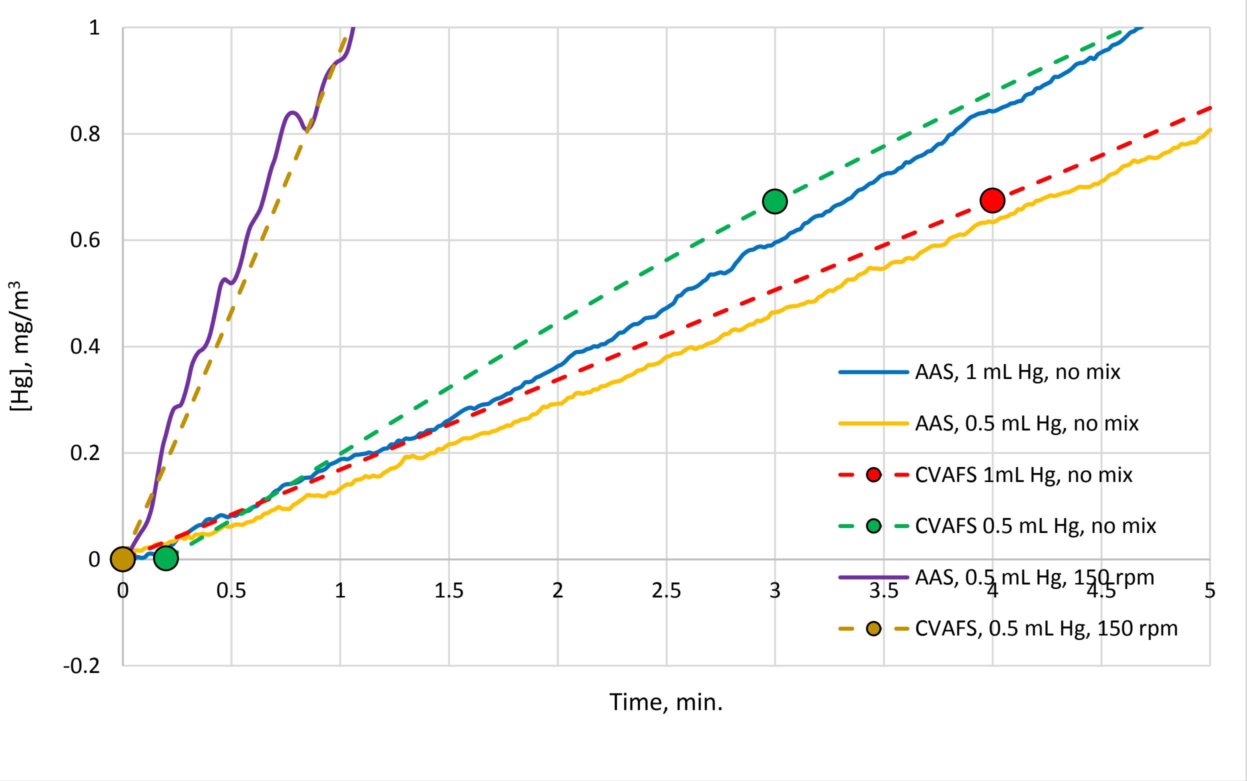

Figure 13. Change of mercury vapour concentration in air vs time produced by undisturbed or mixed mercury in closed 3 L reaction flask measured by CVAFS and AAS methods, first 5 min period, 20°C.

Taking into account the very small value of maximum permissible concentration of mercury vapours in the air (ACGIH: 0.1mg/m^3 not to be exceeded at any time) [15] in our experimental conditions a dangerous concentration of mercury vapour formed in less than one minute. The mixing of mercury limited the “safe” period to just several seconds, as it follows from the purple and dashed yellow traces in Figure 13.

Conclusions for Task 1:

- CVAFS and modified AAS methods were suitable for analysis of mercury vapours in the air. The results of both methods were in excellent agreement with each other.

- Mercury evaporated into the air relatively fast, and it reached a saturation point in 8 hours when mercury is undisturbed (3L round flask, 20°C, and atmospheric pressure).

- The saturated concentration of mercury in the air at 20°C was 12.9 mg/m^3.

- Fifty percent change of metallic mercury amount resulted in a weak influence on the tendency of mercury to form vapours; however, the mixing (150 rpm) strongly increased mercury evaporation rate by approximately ten times.

- A dangerous concentration of mercury vapours (0.1 mg/m^3) appeared in less than a minute when mercury is undisturbed and much faster when mixed under experimental conditions.

- There were no detectable changes in pressure and temperature inside of the reaction flask during the experiments.

Task 2 – Conversion Efficiency of Metallic Mercury to Mercuric Sulphide Using Sulphur Powder

Experiments on undisturbed mercury vaporization treated with the triple excess of sulphur powder were conducted in two replicates using two analytical techniques. The total experiment time was 120 hours (7200 min) as required by Statement of Work. The AAS spectrometer provided continuous measurement of mercury vapour, while the CVAFS method allowed only periodic measurements. As noted above CVAFS measurements were performed with non-uniform frequency as was agreed. More frequent measurements were made at the beginning of an experiment and less frequent at the end.

The results of undisturbed mercury vaporization treated with the triple excess of sulphur powder are presented in Figure 14 below:

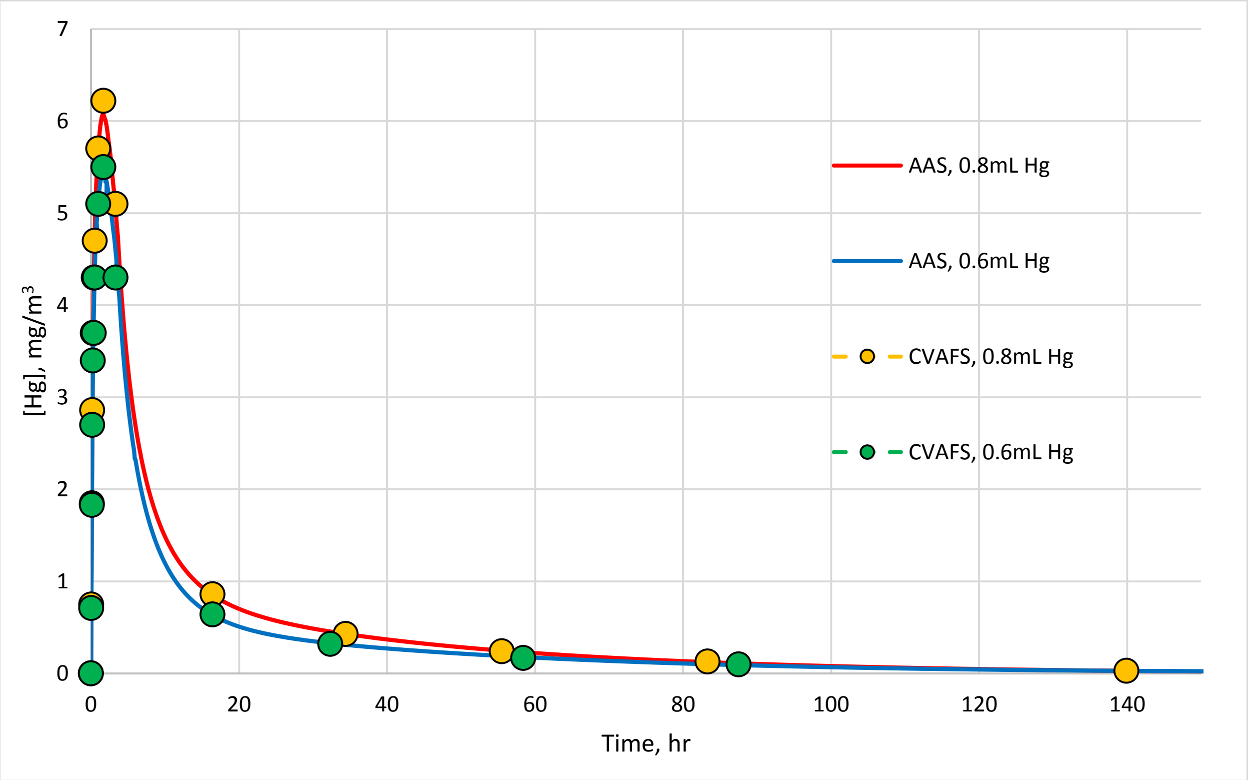

Figure 14. Change of mercury vapour concentration in air vs time produced by undisturbed mercury treated with sulphur powder in closed 3 L reaction flask measured by CVAFS and AAS methods, 20°C.

According to our experimental results presented in Figure 14, mercury vapour concentration jumped high initially, and over time it decreased. A safe level of mercury vapours (below 0.1 mg/m^3) was reached in approximately three days. In Figure 15 data from the same experiments as in Figure 14, but for the period of the first 5 hours (300 minutes) is presented.

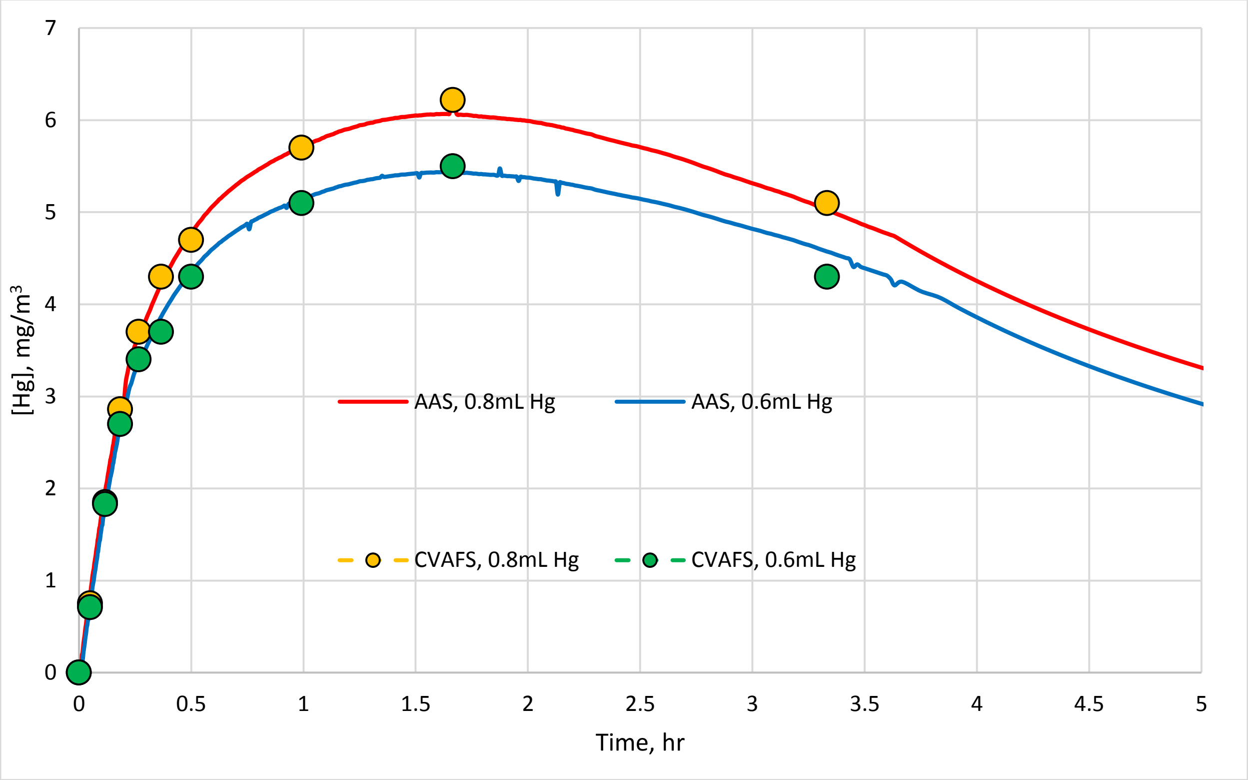

Figure 15. Change of mercury vapour concentration in air vs time produced by undisturbed mercury treated with sulphur powder in closed 3 L reaction flask measured by CVAFS and AAS methods during the 300 min period, 20°C.

Mercury reacted with sulphur, and as a result, the concentration of mercury vapours dropped over time. From the literature, it is known [16] that sulphur slowly evaporates and the equilibrium vapour pressure at 20 °C could reach 38 Pa while mercury pressure is only 0.17 Pa [17] at the same temperature. Observation of the mercury droplet in the reaction vessel showed that the mercury surface, initially shiny as a mirror, became coated with brownish-black mercuric sulphide (HgS), as one can see in Figure 16 below. Such a change of mercury surface means that mercury reacted not only with solid sulphur upon direct contact but also with evaporated sulphur.

Figure 16. A photograph of the undisturbed mercury droplet, exposed to sulphur vapours.

As one can see from Figure 17, where the conversion efficiency of undisturbed mercury versus time is illustrated, the reaction between sulphur powder (including its vapour) and undisturbed mercury was very slow (the efficiency was about 0.5% per day, or 2 – 2.5% per 5 days).

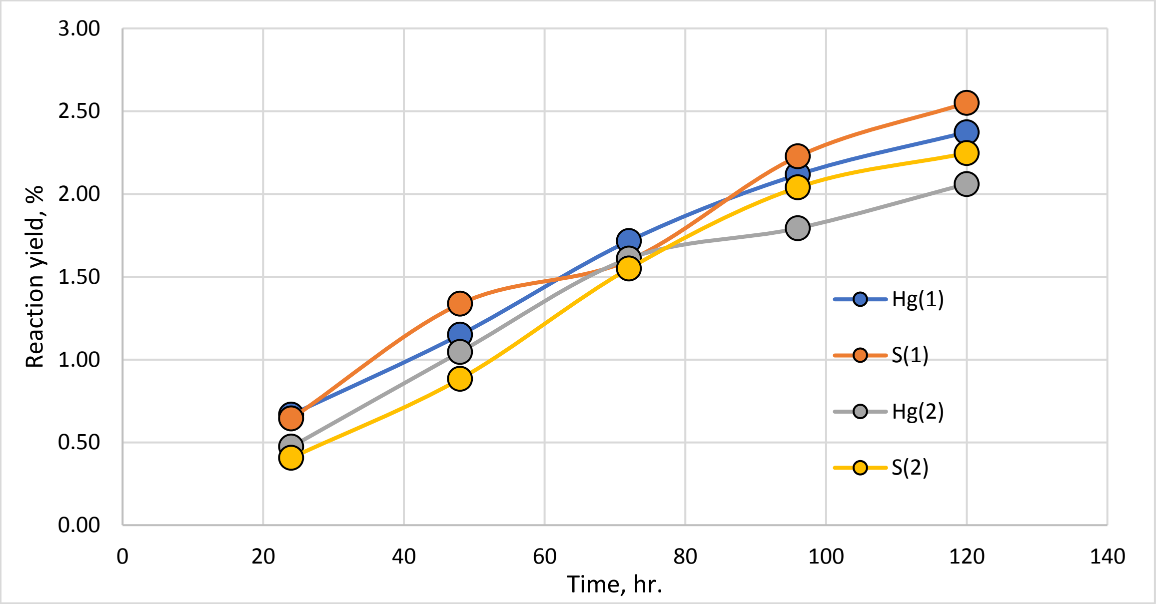

Figure 17. Yields of reaction between undisturbed mercury with triple excess of sulphur powder, calculated by decrease of both reactants, two replicates.

The reaction yield became higher if mercury was continuously mixed with sulphur powder, as shown in Figure 18:

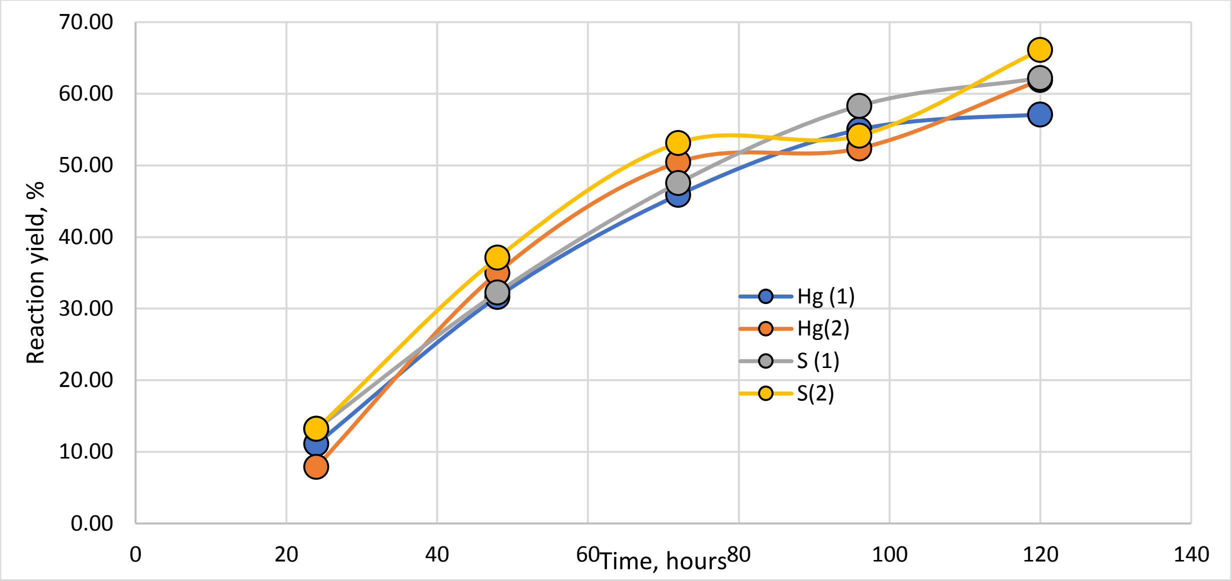

Figure 18. Yields of reactions between mercury with triple excess of sulphur powder, calculated by decrease of both reactants, two replicates, 150 rpm mixing, 20 °C.

The reaction yield was about 15% per day initially, and reached 60% by the fifth day. The yield-time dependency was most likely logarithmic (Figure 19).

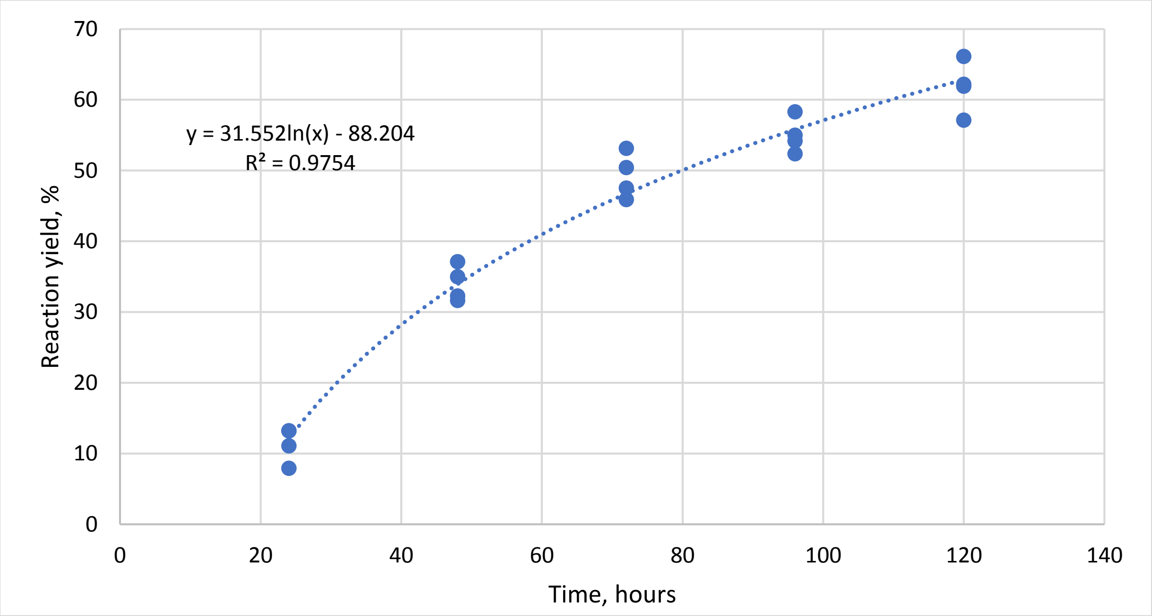

Figure 19. Curve fitted to the reaction yield vs time data points.

Mixing of mercury with sulphur powder significantly increased reaction yield. However, continuous mixing of mercury with sulphur was rupturing HgS coating on mercury drops and exposed a fresh mercury surface to the air (Figure 20), and as a result, promoted mercury evaporation, as shown in Figure 21.

Figure 20. Mercury injected into reaction vessel with sulphur and mixed at 150 rpm.

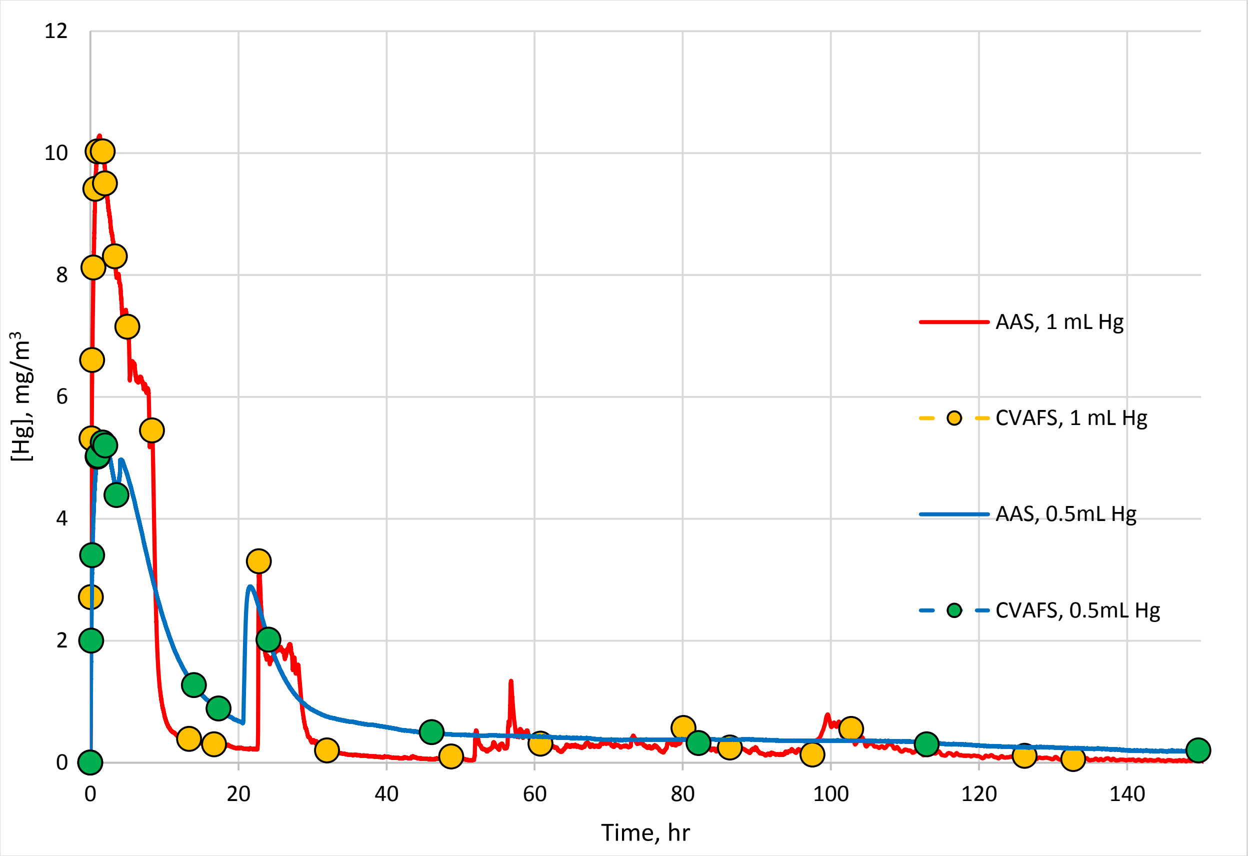

Figure 21. Change of mercury vapour concentration in air vs time produced by mixed mercury treated with sulphur powder in closed 3 L reaction flask measured by CVAFS and AAS methods, 150 rpm, and 20°C.

Figure 22 shows the data from the same experiment as in Figure 21, but for the period of the first 12 hours. Compared with undisturbed conditions (Figure 15 vs. Figure 22), if mixing was applied the concentration of mercury vapours remained at a dangerous level for a more extended period.

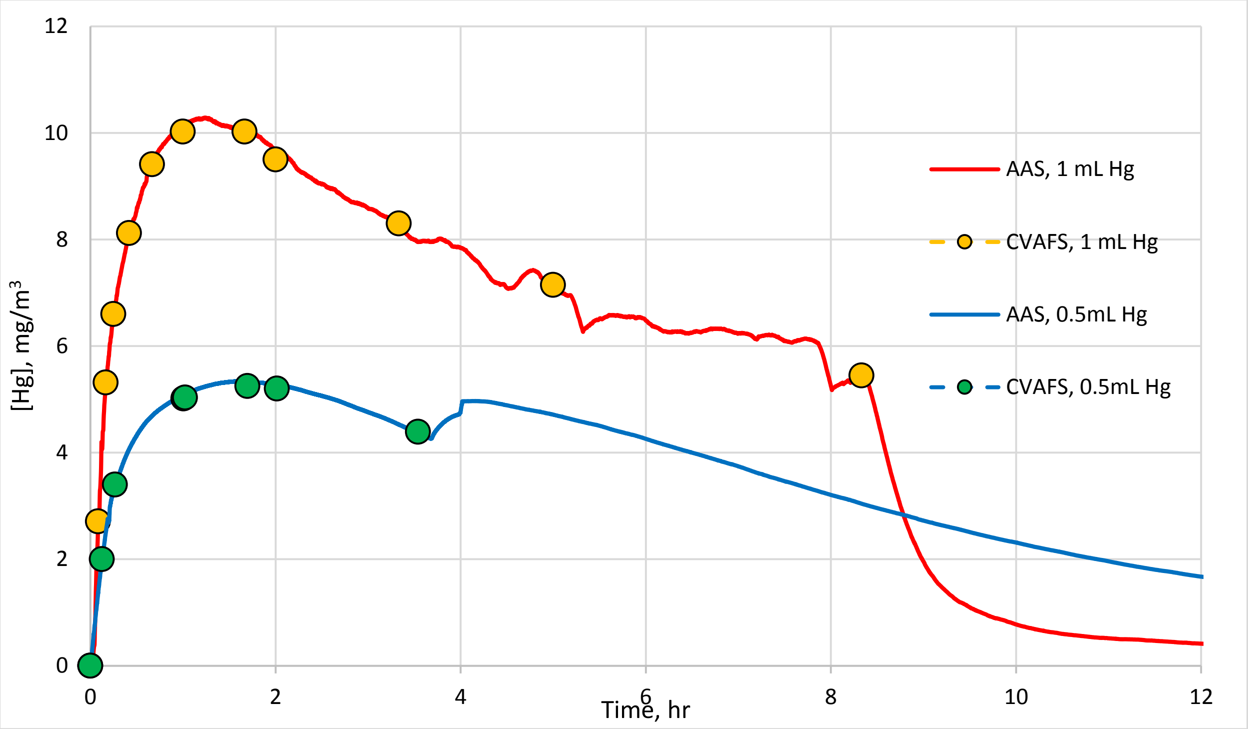

Figure 22. Change of mercury vapour concentration in air vs time produced by mixed mercury treated with sulphur powder in closed 3 L reaction flask measured by CVAFS and AAS methods, 150 rpm, and 20°C.

In all experiments, sulphur was placed into the reactor first, and then mercury was injected under the sulphur layer as a single drop trough a Teflon® capillary. If undisturbed, mercury did not form a homogenous mixture with sulphur; mercury did not wet or penetrate sulphur powder. As a result, mercury and sulphur remained as two separate phases - a liquid drop of mercury and sulphur powder around it. The thickness of sulphur powder on the top of the mercury drop was approximately 1 mm (if undisturbed). Despite the presence of sulphur, the mercury evaporated during several first hours of experiments. The mercury vapour concentration in the presence of sulphur was lower compared with pure mercury as shown in Task 1 and illustrated in Figure 14 versus Figure 11. Comparison of these two figures shows that the evaporation of pure, undisturbed mercury happened 2 to 3 times faster than the evaporation of undisturbed mercury in the presence of sulphur. Most likely, the "jump" of mercury vapours concentration in the presence of sulphur occurred because initially mercury had a clean surface and evaporated through a porous layer of powdered sulphur. Over a time, a layer of HgS was built on the mercury surface thereby reducing its evaporation. It should be noted that undisturbed mercury never created saturated vapour in the presence of sulphur (Figure 14).

In experiments with mixing, at the initial period, we observed several clean droplets of mercury on the top of the sulphur layer (Figure 20). As a result, mercury evaporated relatively fast but slower than when pure mercury was mixed (Task 1). Again, in the presence of sulphur, the maximum concentration of mercury vapours did not reach the saturation level (12.9 mg/m^3), compare Figure 22 with Figure 12.

As one can see from Figures 21 and 22, the initial amount of mercury had a substantial influence on mercury vapour concentration. When mixed with sulphur, liquid mercury formed droplets. With a larger amount of mercury, droplets were bigger accordingly. Most likely smaller droplets reacted with sulphur faster, and/or layer of HgS on top of smaller droplets was more stable, which could reduce mercury evaporation.

We obtained a gray powder as a product of reaction of mercury with sulphur powder reacted for five days (Figure 23). Mercuric sulphide was expected as a product of this reaction. It is known, that mercuric sulphide is dimorphic [18] with two crystal forms – red cinnabar (α-HgS) and black metacinnabar (β-HgS).

Figure 23. Mercury – sulphur mixture, reacted for five days, 150 rpm, 20 °C.

The powdered product was examined under a microscope to identify which form of mercuric sulphide was formed in our experiments. The colour indicates that during the reaction of mercury with garden grade sulphur red cinnabar (α-HgS) mercury sulphide was formed (Figure 24).

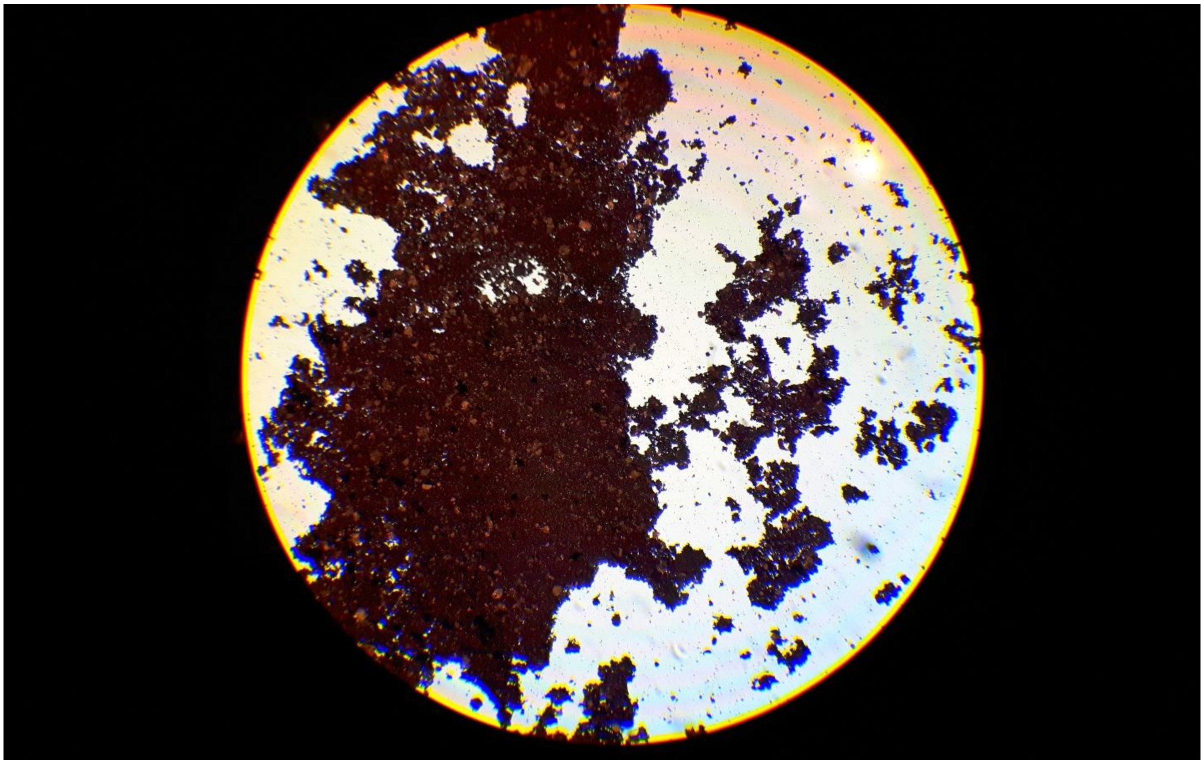

Figure 24. Mercury – sulphur mixture, reacted for five days, 150 rpm, 20 °C, reflective microphotograph, 100X.

In all experiments, the temperature of the reaction mixture and the pressure inside of the reaction vessel were registered; however, no measurable heat effects, under the experimental conditions, and no change in pressure were detected.

Thermodynamically formation of HgS is an exothermic reaction with the standard molar enthalpy of -59 kJ/mol [19] for the α-form of HgS. A negative enthalpy is an indication that a reaction could happen by itself with the energy released as a heat, and a product will be thermodynamically more stable than the initial mixture of reactants, which is suitable for the purpose of this project. However, according to our experiments, $Hg+S \rightarrow HgS$ reaction was slow. To complete the reaction was required more than a week if reactants are mixed, or several months if reactants are not disturbed. The reaction energy release required the same large amount of time and created no measurable heat effects in the experimental conditions. So, the initial rise of mercury vapour concentration may not be related to the heat of the reaction.

Conclusions for Task 2:

- The product of the reaction of mercury with sulphur identified as brownish red cinnabar (α-HgS) mercury sulphide, which known to be a stable and inert compound.

- The reaction of mercury with sulphur was slow, no measurable heat effect (at the experimental conditions) and no change in pressure were detected.

- Sulphur formed a continuous, but fragile, solid shell on mercury surface which reduced mercury evaporation.- Reaction yield was low if mercury-sulphur mixture was not disturbed.

- Reaction yield was higher if mercury mixed with sulphur; however, even mixed, the reaction of mercury with sulphur was not completed in one week.

- Continuous mixing of mercury with sulphur powder resulted in a generation of prolonged and high concentrations of mercury vapours in the surrounding air.

Task 3 – Conversion Efficiency of Metallic Mercury to Mercuric Acetate Using Vinegar and Vinegar-Hydrogen Peroxide Mixture

In this series of experiments, we investigated the conversion efficiency of metallic mercury to mercuric acetate. In the experiments, we combined metallic mercury with household vinegar, which is 5% acetic acid, and after the 60-minutes, we added hydrogen peroxide (H_2O_2) to the reaction mixture. For all experiments, we used a tenfold excess of both hydrogen peroxide and vinegar, calculated from reaction stoichiometry.

In Figure 25 kinetic results of metallic mercury reaction with vinegar (the first 60 minutes) and with the mixture of vinegar with hydrogen peroxide (for the following period from 60-120 minutes) are presented.

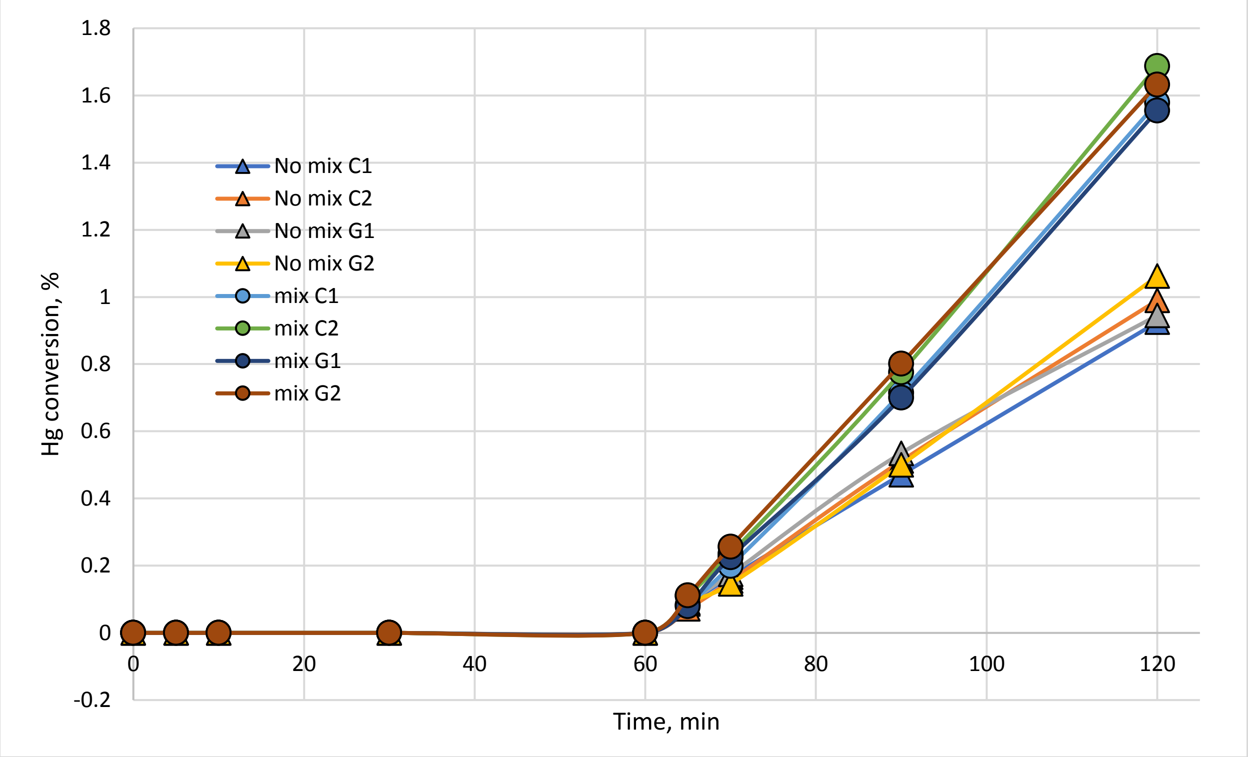

Figure 25. Conversion of mercury into mercuric acetate in vinegar (0-60 min) and in vinegar - hydrogen peroxide mixture (60 - 120 min) with and without mixing, two methods (gravimetric "G" and colorimetric "C") and two replicates.

As seen in Figure 25, mercury did not react with vinegar, which was expected, because vinegar (acetic acid) is not an oxidizing acid, and according to the Metal Activity Series, [19] mercury may not displace hydrogen (proton) in acids. With the addition of hydrogen peroxide to the reaction mixture mercury slowly dissolved and converted into mercuric acetate. This reaction was also expected because of oxidation of mercury to bivalent ion:

$Hg^0 - 2e^- \rightarrow Hg^{+2}$ $E^o = -0.851$ V [19] (1)

This process required an oxidizer, with a standard Oxidation-Reduction Potential E^o (ORP) higher than 0.851 Volts. Hydrogen peroxide and peracetic acid have sufficiently high ORP:

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E^o = 1.776$ V [19] (2)

The ORP potential of peracetic acid/acetic acid was theoretically calculated to be 1.762 V [20]. Despite the high oxidative activity of hydrogen peroxide and peracetic acid, mercury dissolved very slowly. For one hour of the reaction period, the mercury conversion efficiency was only 1% if not mixed, and 1.6% if mixed at 150 rpm. A complete mercury dissolution could take several days. Keeping a vinegar-hydrogen peroxide mixture over a spill area for a sufficient amount of time would be challenging without other engineering controls.

Careful observation of the mercury reaction with mixture vinegar – hydrogen peroxide (compare Figure 26 with Figure 27) showed that the main product of the reaction was oxygen. Apparently, mercury acted as a catalyst of hydrogen peroxide decomposition.

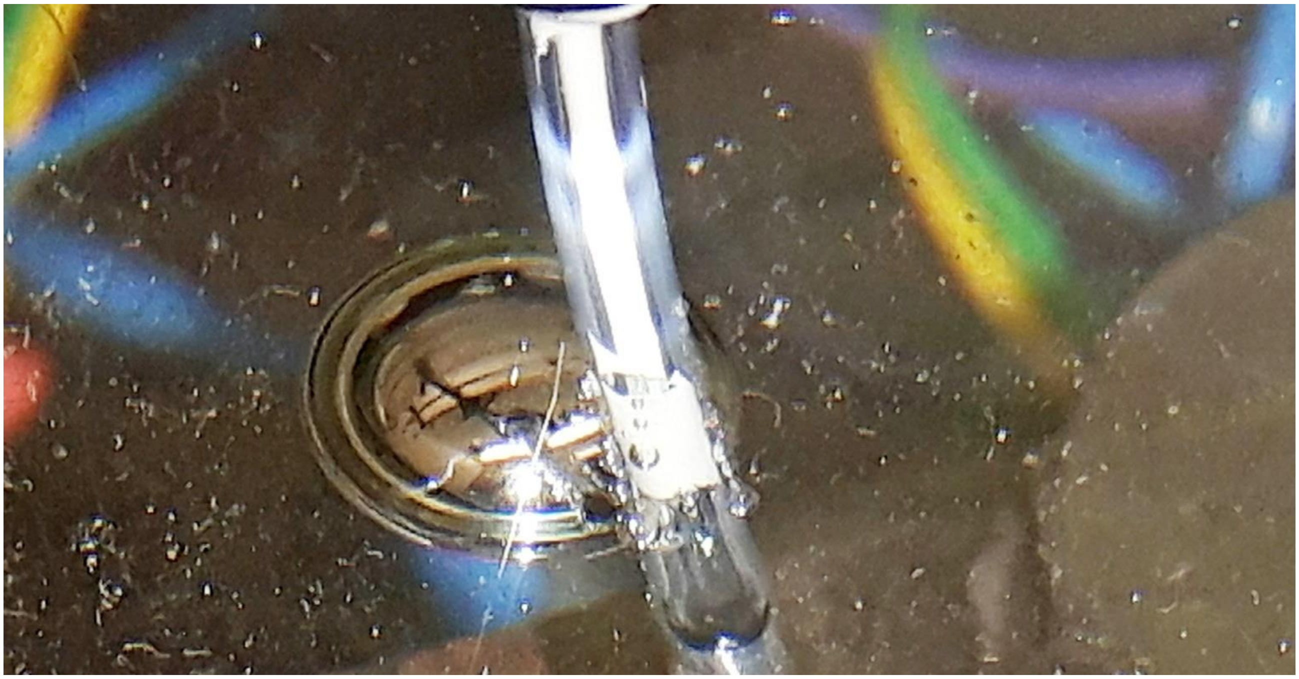

Figure 26. Mercury in vinegar. The temperature sensor placed in front of the mercury droplet.

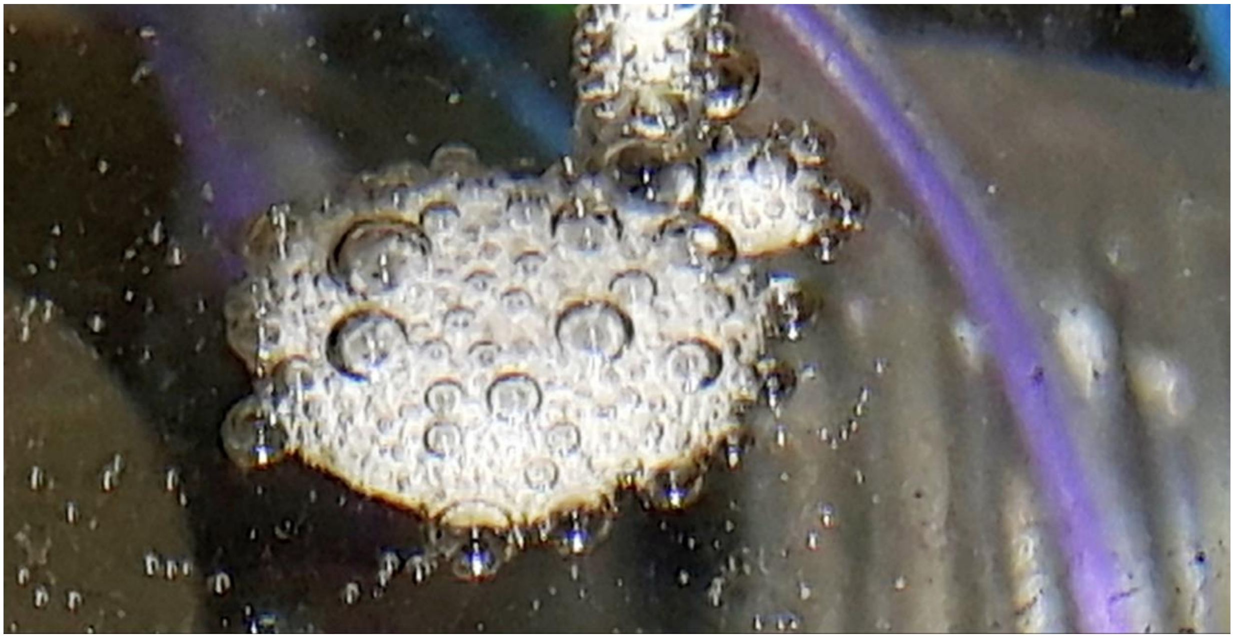

Figure 27. Mercury in vinegar - hydrogen peroxide mixture. Observed intensive oxygen formation.

The intensive release of oxygen from the mercury surface could partially explain the sudden rise of mercury vapour concentration in the air inside of the reactor. The plot of mercury vapour concentration versus time is presented in Figure 28 below.

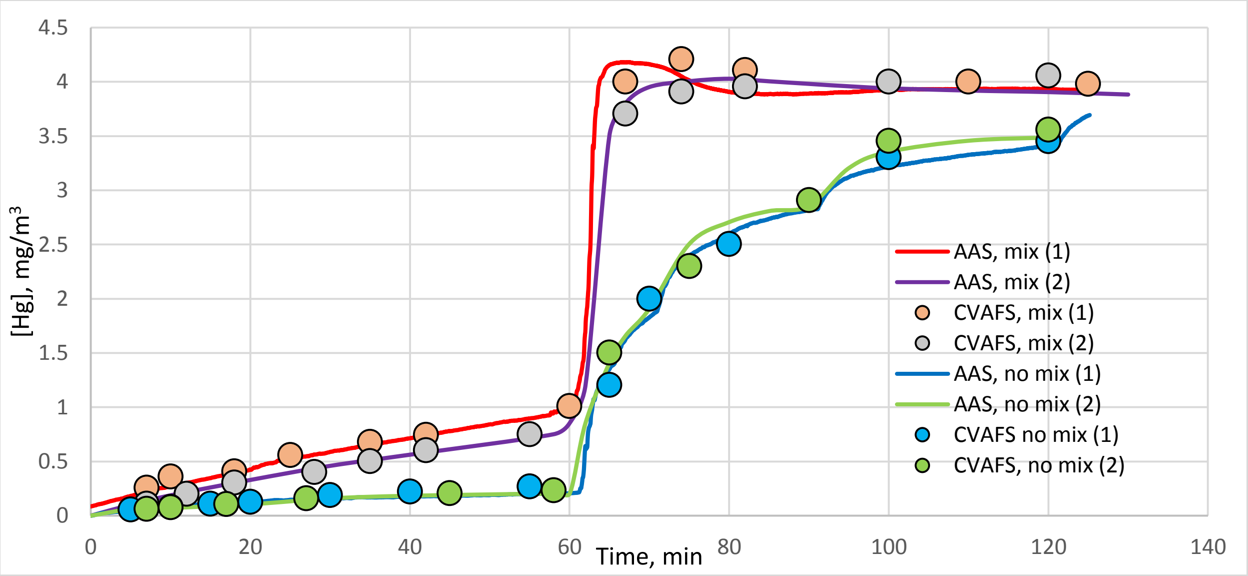

Figure 28. Change of mercury vapour concentration in air vs time. H_2O_2 added at 60-min time point. With and without mixing, two methods (CVAFS and AAS) and two replicates.

During the experiment, vinegar was first poured into the reactor, then mercury was injected under the vinegar layer, so mercury had no direct contact with the air in the reactor. However, vinegar was somehow permeable for mercury vapours, especially if mixed (refer to the first 60-min periods in Figure 28). Addition of hydrogen peroxide at 60-min time point strongly increased mercury evaporation, as it follows from the traces in Figure 28, during the period 60 – 120 min. The bubbles of oxygen, a product of the decomposition of peroxide, resided on the surface of mercury for some time before they floated to the surface. Most likely, the oxygen bubbles saturated with mercury vapours by a direct contact with mercury surface, and accordingly, they delivered mercury vapour to the surface of the vinegar-peroxide mixture, and then mixed with the air. Mixing increased mercury evaporation rate. Interestingly, mercury vapour concentration in the air reached a maximum, approximately 4 mg/m^3 which is about three times lower than the saturation concentration of mercury in the air (compare Figure 28 with Figure 11) at 20°C.

The release of oxygen during the experiments created a noticeable change of pressure in the reactor (Figure 29). Mixing of reaction components increased oxygen release and as a result the pressure. Using ideal gas laws, a final oxygen release of ~ 6 mL for no mix condition and ~10 mL with mixing at 150 rpm was estimated. It is important to note that 10 mL of oxygen saturated with mercury may not create such a high mercury concentration in the 3L reactor, so other mechanisms of mercury transport must exist in the system [mercury → vinegar + hydrogen peroxide → air].

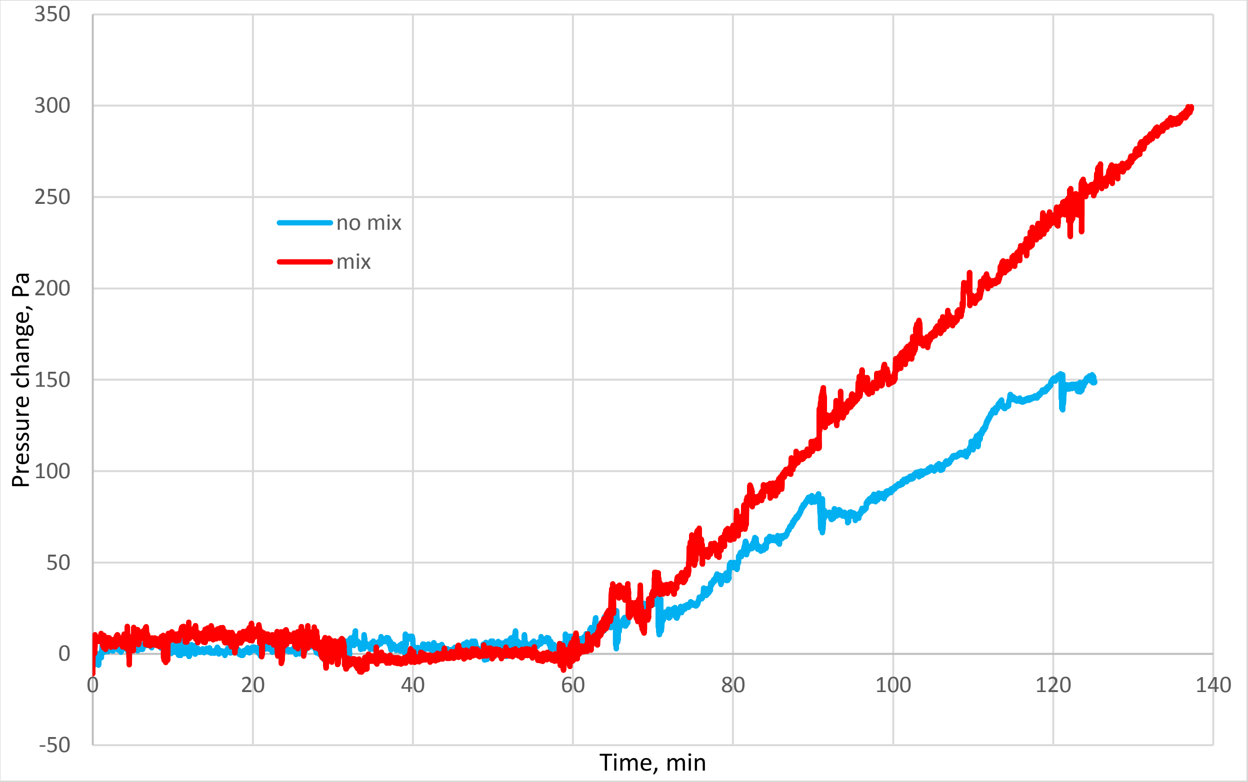

Figure 29. Pressure changes in the reactor. Blue trace - no mixing, red trace - mixing @ 150 rpm. Hydrogen peroxide is added at 60-min. time point.

The temperature was recorded during all experiments; however, no significant heat release was detected in any condition.

Lastly, we measured mercury evaporation from dry mercuric acetate, to check if it was safe to be present in a room after mercury spill remediation. Concentration of mercury vapours in a jar with mercuric acetate was close to the background in the ambient clean air. Note, mercuric acetate is a soluble salt of mercury and is known to be extremely hazardous by skin contact, inhalation and ingestion.

Conclusions for Task 3:

- Mercury did not react with pure vinegar.

- Mercury could be converted into mercuric acetate if treated with vinegar and then with hydrogen peroxide.

- Mercury conversion efficiency with vinegar– hydrogen peroxide mixture was low, approximately 1 – 2% per hour. This yield is higher compared with reaction of mercury with sulphur. However, maintaining a layer of vinegar-hydrogen peroxide over Hg spill over a long period of time would be more challenging.

- Despite the higher conversion efficiency over the sulphur method, however, the practicality of the method seems to pose a problem.

- Mercury penetrated the layer of vinegar and contaminated the air; the mixing accelerated this effect.

- Addition of hydrogen peroxide to vinegar strongly increased mercury evaporation rate and could be dangerous.

- Mercury acted as a catalyst of hydrogen peroxide decomposition, oxygen was released as a product.

- Mercuric acetate in a dry form did not release mercury vapours.

Recommendation of other possible techniques for mercury spill remediation

Based on chemical and physical properties of mercury we are proposing to test a few additional methods of mercury spill remediation.

1. Mercury can form alloys called amalgams with different metals at room temperature. The remediation technique could include a sprinkling of powdered metal, such as zinc or copper over a spill area. It is expected that mercury will form an amalgam with the metal powder. Mercury could either be spread on the surface of the metal or penetrate the metal. In both cases, mercury could lose its liquid property and became attached to or into solid metal particles that could be collected by a vacuum cleaner. It is unclear, if the use of such metal powders may reduce the tendency of mercury to form vapours.
2. Another method worth investigating is the use of calcium hypochlorite (used for pool chlorination) or sodium hypochlorite (bleach) as is or followed by sulphur treatment. It is expected that the hypochlorites will quickly transform mercury into calomel. Use of sulphur may then possibly transform calomel into more stable mercuric sulphide. This approach may result in faster decontamination of mercury spills than using the methods of Tasks 2 and 3 described in this project.
3. We can also test the method, regularly used in laboratories. It includes treatment of mercury spill area with ferric chloride $FeCl_3$ solution. Prepared $FeCl_3$ solution is available to the public, and sold as a printed circuit board etching solution by electronic and amateur stores, such as Addison Électronique.
4. Vinegar – hydrogen peroxide method expected to be efficient; however, mercury catalyzed hydrogen peroxide decomposition which dramatically reduced the method efficiency. We are proposing to use different oxidizer for this method. A much more effective system could be vinegar – potassium permanganate mixture. Potassium permanganate, however, is not available for the public but could be used by contractors or sold in specially designed kits.
5. As a variation of the previous method, we also can test potassium permanganate – hydrochloric acid system. In this mixture, mercury converted to insoluble and not toxic calomel Hg_2Cl_2. Again, applicability of this method is limited by availability of chemicals.
6. Chelating methods could be safe and effective, for example, mercury could be oxidized by hypochlorite and at the same time chelated by calcium citrate, calcium- or sodium ethylenediaminetetraacetate or similar chelating agent into a soluble but not toxic mercury complex salt. Such reactions require an elevated pH. The high pH also stabilizes hypochlorite. There is no such product on the market, but it could be developed and marketed.

7. Reaction of liquid and gaseous mercury with sulphur vapours may contribute to the mitigation of mercury vapour release using sulphur powder and should be studied in more detail.

Conclusions

In this project, we investigated the tendency of mercury to form vapours at ambient temperature and pressure and tested the efficiency of the two prospective methods of mercury spill remediation. The most important findings were:

- Mercury evaporated into the air relatively fast, and it reached a saturation point in 8 hours if mercury is undisturbed. Mixing increased mercury evaporation rate about ten times, and therefore mercury saturation point was reached in just 40 minutes.
- In used experimental conditions, a dangerous concentration of mercury (0.1 mg/m^3) appeared in less than a minute if mercury is undisturbed, and in ~5 seconds if mixed. In some cases the amount of liquid mercury had a small influence on its evaporation rate.
- Mercury reacted with garden grade sulphur resulting in stable red cinnabar (α-HgS) mercury sulphide; however, the reaction was slow and could take several months if undisturbed or several weeks if mixed continuously.
- Sulphur slowly evaporates at room temperature, and it is hypothesized that the resulting vapour reacted with evaporated and liquid mercury. The reaction of sulphur vapour with liquid mercury resulted in the formation of a continuous layer of HgS on the surface of mercury droplets. The continuous layer of HgS was impermeable for mercury vapours. As a result, sulphur reduced the mercury vapour concentration to safe levels in approximately three days, even if several months were required for complete mercury conversion.
- Mercuric sulphide is not soluble and toxic by skin and has low toxicity if ingested [21, 22].
- Mercury did not react with vinegar but slowly dissolved in vinegar-hydrogen peroxide mixture with a yield of approximately 1 – 2% per hour. A slow reaction rate could make this remediation method impractical because it could be challenging to keep a layer of vinegar – hydrogen peroxide mixture over a mercury spill area for a long time.
- Addition of hydrogen peroxide to vinegar strongly increased mercury evaporation rate and could be dangerous.
- The product of mercury conversion with vinegar-hydrogen peroxide mixture was mercuric acetate. As a dry salt mercuric acetate did not form mercury vapours in the air. However, it is known that mercuric acetate is soluble in water and could be toxic to human through contact with hands, for example, if the treated mercury spill area will be washed by hands any time later.

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Appendix: Experimental Raw Data

All weights are in grams.

Abbreviations for Appendix:

A – Optical absorption, a spectrophotometric raw data

[S] – Concentration of sulphur in solution in g/mL

[S], mg/mL – Concentration of sulphur in solution in mg/mL

Wt – Weight

A/[S] – Beer's Law conversion coefficient from A to [S]

List of Tables

Task 1.

The CVAFS method development and validation raw data

Table 1. CVAFS calibration and validation data (manual injection method)

Prepared Standard Hg mg/m^3	Measured CVAFS mg/m^3
12.3132	12.1011
10.02	10.301
5.01	4.5561
3.011	3.3213
1.055	1.2447
0.543	0.4527
0.335	0.3921
0.151	0.0502
0.085	0.0824
0.051	0.0491
0.032	0.0305
0.025	0.0266
0.01	0.0081
0.005	0.0592
0.002	0.0011
0.001	0.0002

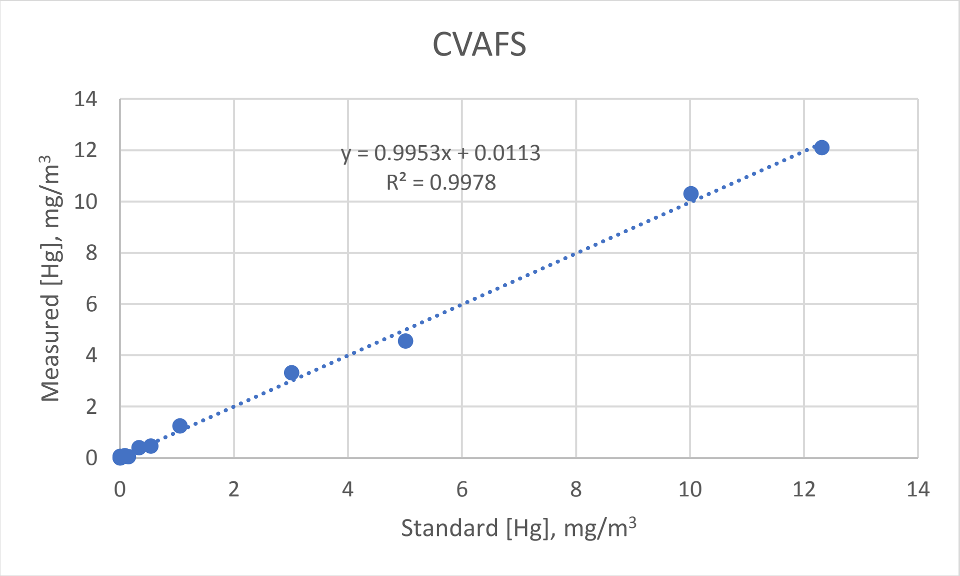

Figure 30. CVAFS calibration and validation data plot

Table 2. CVAFS repeatability for 0.025 mg/m^3 Hg standards

	Prepared	Measured
	Standard Hg	CVAFS
Replicate	mg/m^3	mg/m^3
1	0.025	0.034051
2	0.025	0.010018
3	0.025	0.032912
4	0.025	0.011337
5	0.025	0.024597
6	0.025	0.037568
7	0.025	0.039298
8	0.025	0.022218
9	0.025	0.038108
10	0.025	0.032434
11	0.025	0.017439
12	0.025	0.020766
	Std. Dev	0.011
	Signal/Noise	1210.422

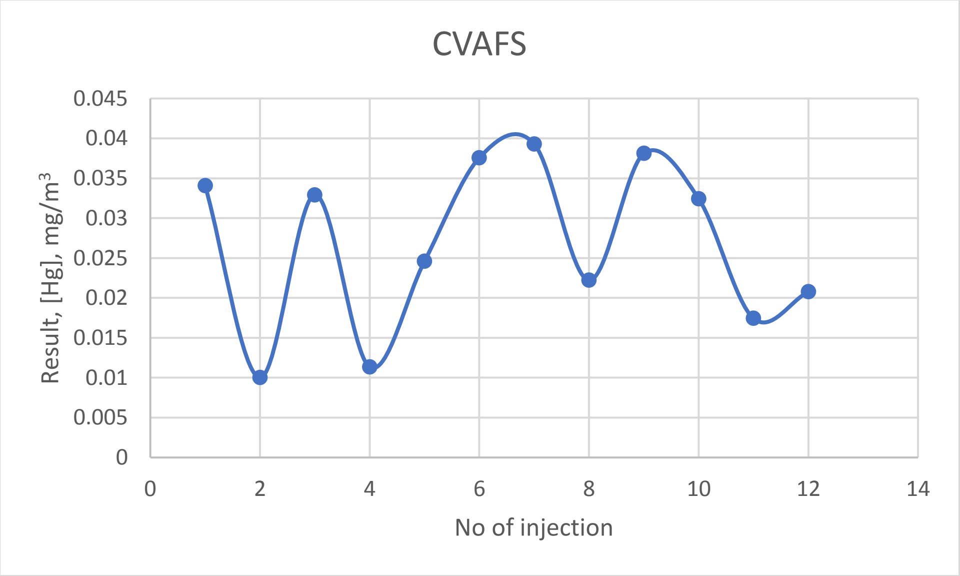

Figure 31. CVAFS repeatability for 0.025 mg/m^3 Hg standards

The CVAFS method validation results:

Range: 13 – 0.01 mg Hg/m^3

Lower Limit of Quantitation is 0.11 mg Hg/m^3 (based on S/N ×10)

Limit of Detection is 0.033 mg Hg/m^3 (based on S/N ×3)

Linearity r^2 is 0.9978

The AAS method development and validation raw data

Table 3. AAS calibration and validation data.

Prepared Standard Hg mg/m^3	Measured AAS mg/m^3
12.3132	12.4343
10.02	10.006
5.01	5.0021
3.011	3.0121
1.055	1.0581
0.543	0.5621
0.335	0.3381
0.151	0.1518
0.085	0.0831
0.051	0.0501
0.032	0.0331
0.025	0.0248
0.01	0.0098
0.005	0.0061
0.002	0.0012
0.001	0.0011

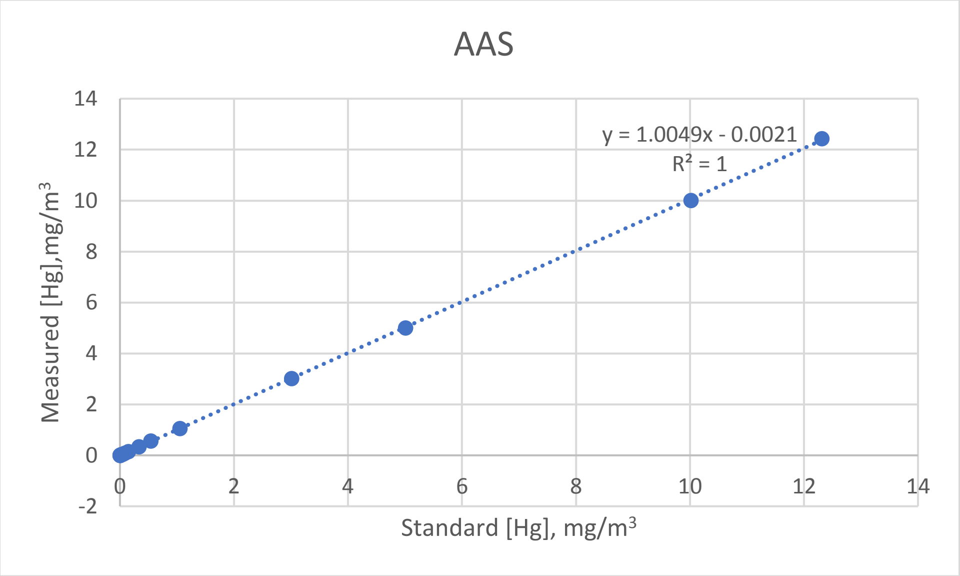

Figure 32. AAS calibration and validation data.

Table 4. AAS repeatability for 0.025 mg/m^3 Hg standards

	Prepared	Measured
	Standard Hg	AAS
Replicate	mg/m^3	mg/m^3
1	0.025	0.024070
2	0.025	0.025208
3	0.025	0.024200
4	0.025	0.026496
5	0.025	0.024423
6	0.025	0.026844
7	0.025	0.026512
8	0.025	0.025860
9	0.025	0.023816
10	0.025	0.026287
11	0.025	0.023504
12	0.025	0.023166
	Std. Dev	0.00124
	Signal/Noise	10476.982

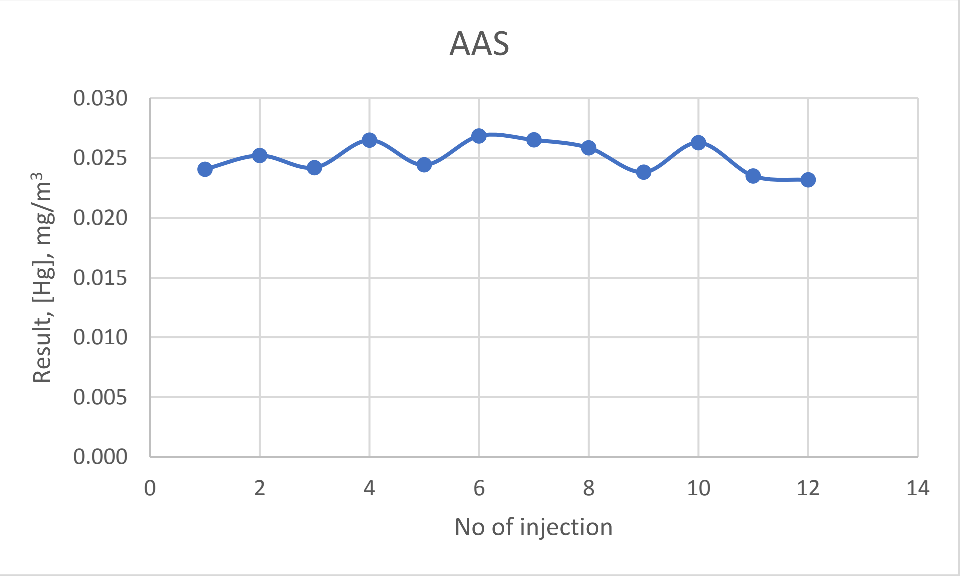

Figure 33. AAS repeatability for 0.025 mg/m^3 Hg standards

The AAS method validation results:

Range: 13 – 0.001 mg Hg/m^3

Lower limit of quantitation is 0.012 mg Hg/m^3 (based on S/N ×10)

Limit of detection is 0.0036 mg Hg/m^3 (based on S/N ×3)

Linearity r^2 is better than 0.9999

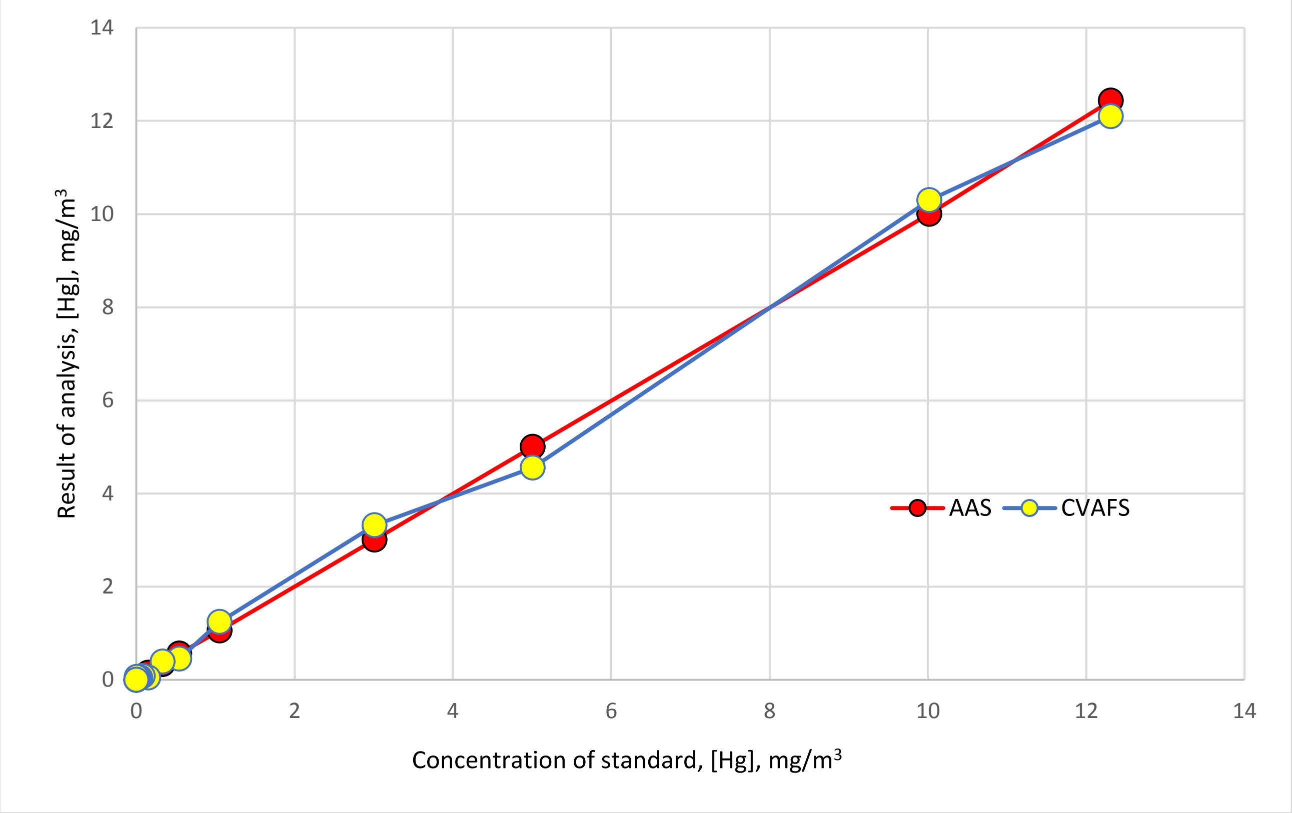

Figure 34. Performance of AAS compared to CVAFS

Task 1 experimental raw data: CVAFS and AAS mercury vapour analysis without mixing

Table 5. Exact weight of mercury, used in no-mix experiment #1 (1 mL Hg)

	Weight, g
Syringe initial	2.5321
Syringe with Hg	15.996
Syringe after	2.5448
Hg injected	13.4512
Hg left in syringe	0.0127

Referred below as “1 mL Hg”

Table 6. Mercury vapour concentration measured by CVAFS; no-mix experiment #1; 1 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0.00	0.000
4	0.07	0.674
6	0.10	0.996
10	0.17	1.449
13	0.22	2.096
18	0.30	2.947
21	0.35	3.646
26	0.43	4.355
30	0.50	4.908
40	0.67	6.058
55	0.92	7.528
65	1.08	8.195
74	1.23	8.822
90	1.50	9.634
100	1.67	10.054
110	1.83	10.485
120	2.00	10.929
180	3.00	12.270
240	4.00	12.488
300	5.00	12.688
720	12.00	12.801
1080	18.00	12.851
1200	20.00	12.851
1440	24.00	12.951
2880	48.00	12.751
4320	72.00	12.991
5760	96.00	12.971
7200	120.00	12.751

Table 7. Mercury vapour concentration measured by AAS; no-mix experiment #1; 1 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0	0
0.5	0.008	0.0826
1	0.017	0.1880
3	0.050	0.5957
5	0.083	1.0652
10	0.167	1.9584
20	0.333	3.8465
30	0.500	5.3036
60	1	8.2020
120	2	10.9682
180	3	12.1307
300	5	12.7455
600	10	12.8526
1440	24	12.8507
2160	36	12.8534
2880	48	12.85046
3600	60	12.8549
4320	72	12.8529
5040	84	12.8538
5760	96	12.8512
6480	108	12.8508
7200	120	12.8535

Table 8. Exact weight of mercury, used in no-mix experiment #2 (0.5 mL Hg)

	Weight, g
Syringe initial	2.5245
Syringe with Hg	8.9818
Syringe after	2.5437
Hg injected	6.4381
Hg left in syringe	0.0192

Referred below as “0.5 mL Hg”

Table 9. Mercury vapour concentration measured by CVAFS; no-mix experiment #2; 0.5 mL Hg

Time, min	Time, hr	Hg mg/m^3
0.2	0.00	0.002
3	0.05	0.672
6	0.10	1.220
9	0.15	1.466
15	0.25	2.421
20	0.33	3.179
25	0.42	3.780
31	0.52	4.528
40	0.67	5.340
44	0.73	5.913
48	0.80	6.405
55	0.92	6.783
62	1.03	7.514
79	1.32	8.430
140	2.33	11.528
160	2.67	12.047
195	3.25	12.472
203	3.38	12.502
260	4.33	12.412
400	6.67	12.695
880	14.67	12.850
1300	21.67	12.750
2300	38.33	12.710
3500	58.33	12.721
5500	91.67	12.790
7200	120.00	12.990

Table 10. Mercury vapour concentration measured by AAS; no-mix experiment #2; 0.5 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0	0
0.5	0.008	0.0620
1	0.017	0.1331
3	0.050	0.4642
5	0.083	0.8070
10	0.167	1.6451
20	0.333	3.0058
30	0.500	4.2967
60	1	7.1867
120	2	10.4977
180	3	12.2006
300	5	12.7115
600	10	12.7977
1440	24	12.8007
2160	36	12.8023
2880	48	12.8006
3600	60	12.8021
4320	72	12.7997
5040	84	12.7995
5760	96	12.7983
6480	108	12.8023
7200	120	12.8002

Task 1 experimental raw data: temperature and pressure change in experiments without mixing

Table 11. Temperature and change of pressure during two experiments (#1 – 1 mL Hg and #2 – 0.5 mL Hg)

		No mix experiment #1 - 1 mL Hg		No mix experiment #2 - 0.5 mL Hg	
Time, min	Time, hr	Temperature, °C	Pressure change, Pa	Temperature, °C	Pressure change, Pa
0	0	20.62	0.00	20.10	0.66
0.5	0.008	20.62	0.01	20.12	1.04
1	0.017	20.64	0.21	20.15	2.66
3	0.050	20.64	0.42	20.16	1.88
5	0.083	20.62	0.62	20.18	0.66
10	0.167	20.64	0.61	20.21	2.27
20	0.333	20.64	1.24	20.21	0.44
30	0.500	20.66	1.44	20.18	1.80
60	1	20.67	2.04	20.16	0.62
120	2	20.64	0.61	20.14	1.39
180	3	20.65	1.02	20.11	1.50
300	5	20.66	1.22	20.09	2.95
600	10	20.67	1.03	20.07	3.02
1440	24	20.68	0.01	20.03	0.42
2160	36	20.69	0.21	20.00	1.83
2880	48	20.65	2.04	19.97	1.58
3600	60	20.68	1.22	19.94	0.99
4320	72	20.68	0.20	19.94	1.68
5040	84	20.70	2.24	19.94	0.40
5760	96	20.72	3.28	19.94	0.53
6480	108	20.73	2.67	19.95	1.46
7200	120	20.73	2.87	19.96	2.45

Task 1 raw data: CVAFS and AAS mercury vapour analysis with mixing at 150 rpm

Table 12. Exact weight of mercury, used in mix experiment #1 (1 mL Hg)

	Weight, g
Syringe initial	2.5241
Syringe with Hg	15.651
Syringe after	2.5256
Hg injected	13.1254
Hg left in syringe	0.0015

Referred below as “1 mL Hg”

Table 13. Mercury vapour concentration measured by CVAFS; mix experiment #1; 1 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0.00	0
3	0.05	3.408
8	0.13	6.757
12	0.20	8.670
15	0.25	9.914
20	0.33	11.628
30	0.50	11.959
44	0.73	12.596
60	1.00	12.784
80	1.33	12.641
12	0.20	12.693
120	2.00	12.921
160	2.67	12.893
320	5.33	12.873
560	9.33	12.862
1440	24.00	12.969
2880	48.00	12.917
4320	72.00	13.048
5760	96.00	12.727
7200	120.00	12.810

Table 14. Mercury vapour concentration measured by AAS; mix experiment #1; 1 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0	0
0.5	0.008	0.5227
1	0.017	0.9393
3	0.050	2.7698
5	0.083	4.2750
10	0.167	7.2487
20	0.333	10.0837
30	0.500	12.0697
60	1	12.8033
120	2	12.8031
180	3	12.8142
300	5	12.8507
600	10	12.8540
1440	24	12.8536
2160	36	12.8541
2880	48	12.8548
3600	60	12.8549
4320	72	12.8557
5040	84	12.8521
5760	96	12.8526
6480	108	12.8560
7200	120	12.8519

Table 15. Exact weight of mercury, used in mix experiment #2 (0.5 mL Hg)

	Weight, g
Syringe initial	2.5191
Syringe with Hg	9.2737
Syringe after	2.5286
Hg injected	6.7451
Hg left in syringe	0.0095

Table 16. Mercury vapour concentration measured by CVAFS; mix experiment #2; 0.5 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0.00	0.0000
4	0.07	3.6012
10	0.17	6.8087
15.5	0.26	8.8432
21	0.35	10.0312
26	0.43	11.4948
30	0.50	11.9000
45	0.75	12.7222
60	1.00	12.7341
72	1.20	12.7962
80	1.33	12.8154
120	2.00	12.8018
160	2.67	12.8152
320	5.33	12.8412
554	9.23	12.8517
1440	24.00	12.8544
2881	48.02	12.8611
4322	72.03	12.8511
5760	96.00	12.8538
7200	120.00	12.8501

Table 17. Mercury vapour concentration measured by AAS; mix experiment #2; 0.5 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0	0
0.5	0.008	0.5192
1	0.017	0.9384
3	0.050	2.7824
5	0.083	4.2880
10	0.167	7.2551
20	0.333	10.0823
30	0.500	12.0227
60	1	12.8099
120	2	12.8022
180	3	12.8155
300	5	12.8521
600	10	12.8558
1440	24	12.8529
2160	36	12.8533
2880	48	12.8543
3600	60	12.8543
4320	72	12.8538
5040	84	12.8510
5760	96	12.8513
6480	108	12.8544
7200	120	12.8509

Task 1 experimental raw data: temperature and pressure change in experiments with mixing at 150 rpm

Table 18. Temperature and change of pressure during two experiments (#1 – 1 mL Hg @ 150 rpm and #2 – 0.5 mL Hg @ 150 rpm)

		Experiment with mixing #1 - 1 mL Hg		Experiment with mixing #2 - 0.5 mL Hg	
Time, min	Time, hr	Temperature, °C	Pressure change, Pa	Temperature, °C	Pressure change, Pa
0	0	20.66	2.03	20.21	0.94
0.5	0.008	20.67	1.23	20.17	2.44
1	0.017	20.66	0.97	20.12	2.07
3	0.050	20.67	1.21	20.14	1.08
5	0.083	20.68	3.32	20.16	1.15
10	0.167	20.69	2.40	20.17	2.12
20	0.333	20.71	2.16	20.18	1.99
30	0.500	20.74	2.08	20.19	1.31
60	1	20.77	1.96	20.21	0.70
120	2	20.78	2.19	20.23	2.98
180	3	20.78	2.68	20.15	0.86
300	5	20.77	3.70	20.13	0.50
600	10	20.78	1.66	20.19	0.26
1440	24	20.78	3.05	20.23	2.30
2160	36	20.76	1.65	20.25	2.88
2880	48	20.76	1.72	20.26	1.32
3600	60	20.77	3.67	20.23	0.78
4320	72	20.78	1.90	20.21	2.08
5040	84	20.79	3.19	20.17	2.52
5760	96	20.81	2.81	20.11	2.64
6480	108	20.85	3.71	20.05	3.02
7200	120	20.87	0.95	20.03	1.15

Task 2.

Spectrophotometric method of sulphur analysis calibration and validation raw data

Optimization of analytical wavelength of the method based on linearity:

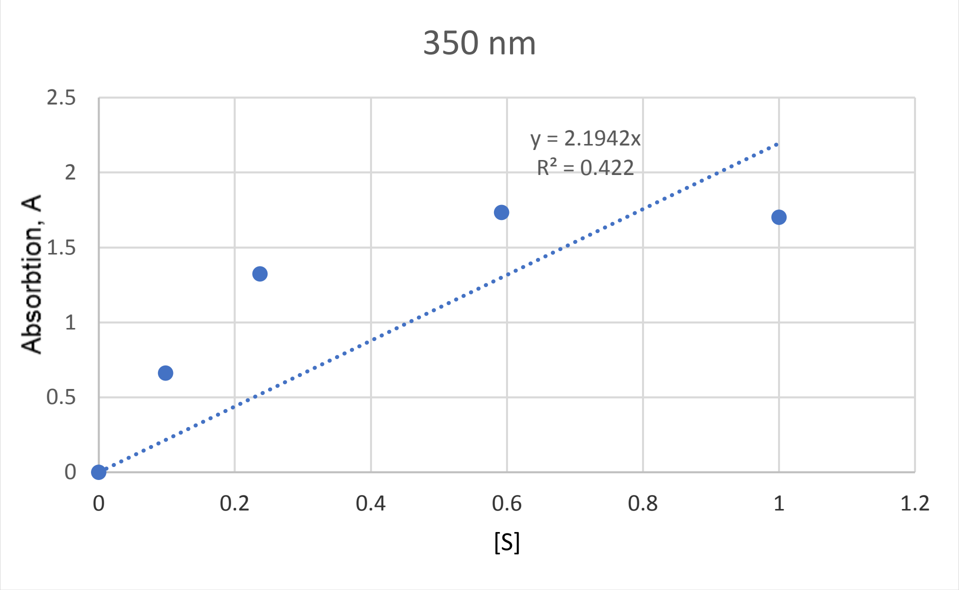

Figure 35. Calibration and validation of sulphur analysis at 350 nm

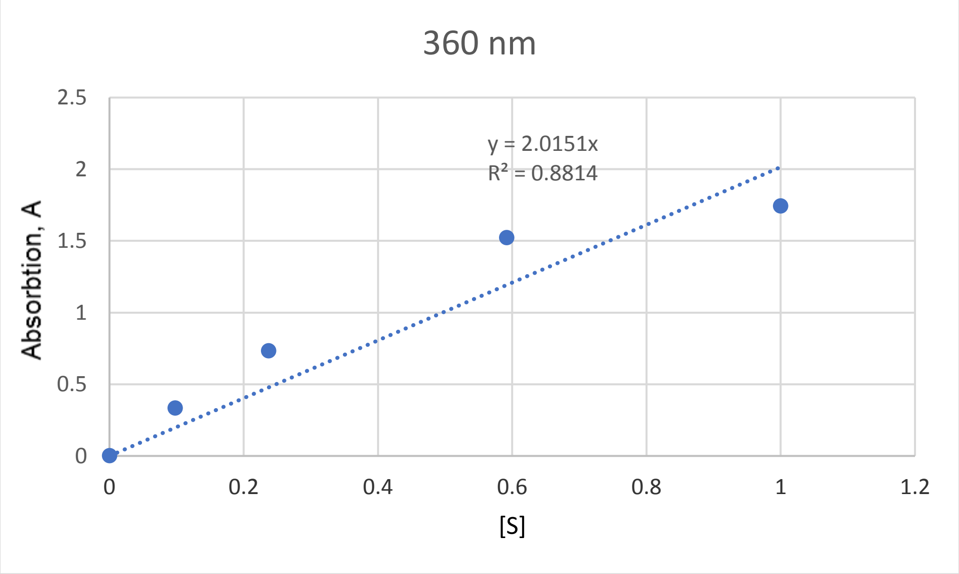

Figure 36. Calibration and validation of sulphur analysis at 360 nm

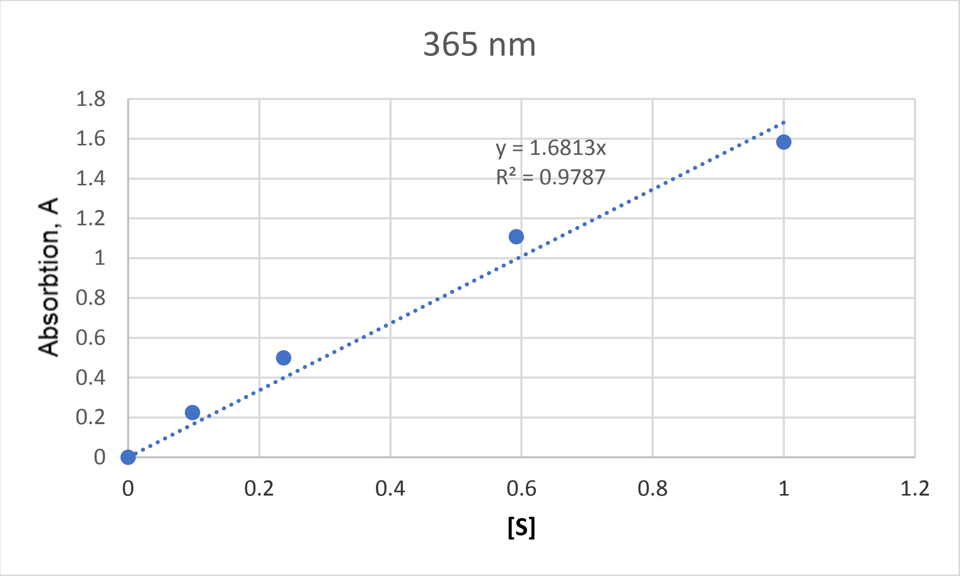

Figure 37. Calibration and validation of sulphur analysis at 365 nm

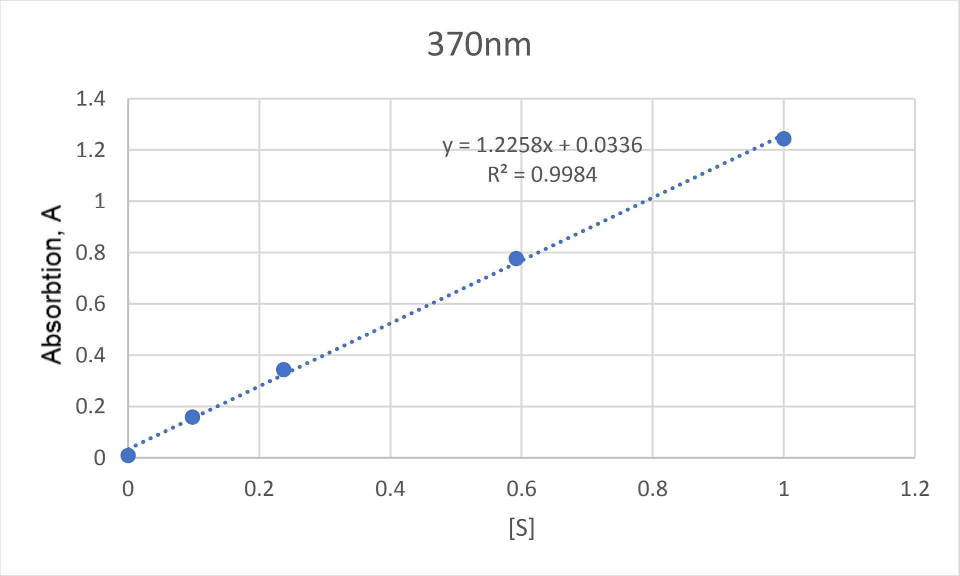

Figure 38. Calibration and validation of sulphur analysis at 370 nm

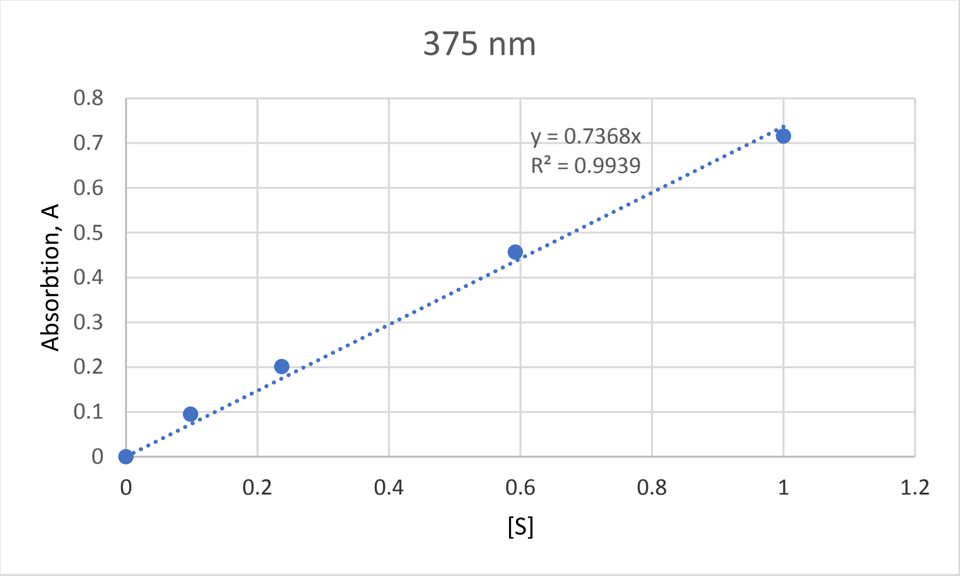

Figure 39. Calibration and validation of sulphur analysis at 375 nm

Best analytical wavelength is 370 nm; reference is 625 nm;

Linearity at 370 nm (r^2) is 0.9984

Range at 370 nm: 0 – 100%

Limit of Detection is 0.006% (S/N ×3)

Lower Limit of Quantitation is 0.02% (S/N ×10)

Task 2 experimental raw data: Analysis of commercial sulphur purity

Table 19. Analysis of commercial sulphur purity, initial data

Name	Weight	Vol solvent	A (370nm)	[S] mg/mL	[S]/A
99 % Sulphur (Std)	0.4183	50	1.107	8.366	7.557362
Commercial sulphur	0.4538	50	1.123	8.486918	

Table 20.Analysis of commercial sulphur purity - result

Pure sulphur in commercial product	0.4243	g
Purity of garden grade commercial sulphur	93.509	%

Task 2 experimental raw data: Yield of reaction by sulphur and by mercury without mixing

Table 21. Yield of Hg+S reaction, calculated by mercury, no mixing, 0.8 mL Hg

Time, hr.	Hg weight initial	Hg left in syringe	Hg Wt injected	Hg recover.	Hg conv.	Yield %
24	10.8124	0.0121	10.8003	10.7283	0.0720	0.667
48	10.6371	0.0047	10.6324	10.5101	0.1223	1.150
72	10.7552	0.0024	10.7528	10.5682	0.1846	1.717
96	10.8237	0.0032	10.8205	10.5915	0.2290	2.116
120	10.8109	0.0056	10.8053	10.5489	0.2564	2.373

Table 22. Yield of Hg+S reaction, calculated by sulphur, no mixing, 0.8 mL Hg

Hg Wt ~ 10g		Sulphur 3x excess =		4.8 g	A/[S]=	23.450
Time, hr.	S initial	A	[S]	S recov.	S conv.	Yield %
24	4.8231	1.1237	0.048	4.792	0.031	0.647
48	4.8155	1.1141	0.048	4.751	0.065	1.340
72	4.8510	1.1193	0.048	4.773	0.078	1.605
96	4.8011	1.1008	0.047	4.694	0.107	2.226
120	4.8144	1.1002	0.047	4.692	0.123	2.549

Table 23. Yield of Hg+S reaction, calculated by mercury, no mixing, 0.6 mL Hg

Time, hr.	Hg weight initial	Hg left in syringe	Hg Wt injected	Hg recover.	Hg conv.	Yield %
24	8.1124	0.0081	8.1043	8.0659	0.0384	0.474
48	8.1247	0.0077	8.117	8.032	0.0850	1.047
72	8.2411	0.0057	8.2354	8.1028	0.1326	1.610
96	8.1541	0.0064	8.1477	8.0015	0.1462	1.794
120	8.0255	0.0082	8.0173	7.8521	0.1652	2.061

Table 24. Yield of Hg+S reaction, calculated by sulphur, no mixing, 0.6 mL Hg

Hg Wt ~ 8g		Sulphur 3x excess =		3.8 g	A/[S]=	23.450
Time, hr.	S initial	A	[S]	S recov.	S conv.	Yield %
24	3.8124	0.8904	0.038	3.797	0.015	0.404
48	3.8211	0.8881	0.038	3.787	0.034	0.887
72	3.8158	0.8809	0.038	3.757	0.059	1.554
96	3.8144	0.8762	0.037	3.736	0.078	2.043
120	3.8021	0.8715	0.037	3.716	0.086	2.254

Task 2 raw data: Yield of reaction by sulphur and by mercury with mixing at 150 rpm

Table 25. Yield of Hg+S reaction, calculated by mercury, with mixing, 0.8 mL Hg

Time, hr.	Hg weight initial	Hg left in syringe	Hg Wt injected	Hg recover.	Hg conv.	Yield %
24	10.8351	0.0021	10.833	9.6304	1.2026	11.101
48	10.8022	0.0561	10.7461	7.3468	3.3993	31.633
72	10.8401	0.0101	10.83	5.8604	4.9696	45.887
96	10.7982	0.0092	10.789	4.8536	5.9354	55.013
120	10.8159	0.0075	10.8084	4.6359	6.1725	57.108

Table 26. Yield of Hg+S reaction, calculated by sulphur, with mixing, 0.8 mL Hg

Hg Wt ~ 10g		Sulphur 3x excess =		4.8 g	A/[S]=	23.450
Time, hr.	S initial	A	[S]	S recov.	S conv.	Yield %
24	4.8052	0.9781	0.042	4.171	0.634	13.198
48	4.8587	0.7719	0.033	3.292	1.567	32.252
72	4.8321	0.5944	0.025	2.535	2.297	47.543
96	4.8451	0.4736	0.020	2.020	2.825	58.316
120	4.8001	0.4256	0.018	1.815	2.985	62.190

Table 27. Yield of Hg+S reaction, calculated by mercury, with mixing, 0.6 mL Hg

Time, hr.	Hg weight initial	Hg left in syringe	Hg Wt injected	Hg recover.	Hg conv.	Yield %
24	8.1135	0.0085	8.105	7.4633	0.6417	7.917
48	8.1981	0.0105	8.1876	5.3227	2.8649	34.991
72	8.1554	0.0084	8.147	4.038	4.1090	50.436
96	8.1352	0.0011	8.1341	3.8734	4.2607	52.381
120	8.1554	0.0031	8.1523	3.1059	5.0464	61.902

Table 28. Yield of Hg+S reaction, calculated by sulphur, with mixing, 0.6 mL Hg

Hg Wt ~ 8g		Sulphur 3x excess =		3.8 g	A/[S]=	23.450
Time, hr.	S initial	A	[S]	S recov.	S conv.	Yield %
24	3.8021	0.7739	0.033	3.300	0.502	13.200
48	3.8125	0.5622	0.024	2.397	1.415	37.116
72	3.7958	0.4171	0.018	1.779	2.017	53.141
96	3.8215	0.4107	0.018	1.751	2.070	54.170
120	3.8012	0.302	0.013	1.288	2.513	66.120

Task 2 experimental raw data: CVAFS and AAS analysis of mercury vapour produced by liquid mercury treated with sulphur without mixing

Table 29. Exact weight of mercury, used in no-mix experiment #1 (0.8 mL Hg)

	Weight, g
Syringe initial Wt	2.5321
Syringe with Hg	13.3619
Syringe after	2.5338
Hg injected	10.8281
Hg left in syringe	0.0017

Table 30. Mercury vapour concentration measured by CVAFS; no-mix experiment #1; 0.8 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0	0.001
3	0.05	0.749
7	0.12	1.851
11	0.18	2.856
16	0.27	3.699
22	0.37	4.304
30	0.50	4.703
59.5	0.99	5.704
100	1.67	6.219
200	3.33	5.100
985	16.42	0.864
2065	34.42	0.432
3330	55.50	0.239
5000	83.33	0.134
8395	139.92	0.031
10875	181.25	0.007
12180	203.00	0.001

Table 31. Mercury vapour concentration measured by AAS; no-mix experiment #1; 0.8 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0	0
0.5	0.008	0.013
1	0.017	0.142
3	0.050	0.736
5	0.083	1.305
10	0.167	2.464
20	0.333	3.708
30	0.500	4.351
60	1	5.154
120	2	5.376
180	3	4.819
300	5	2.920
600	10	1.197
1440	24	0.426
2160	36	0.299
2880	48	0.226
3600	60	0.188
4320	72	0.130
5040	84	0.099
5760	96	0.075
6480	108	0.057
7200	120	0.043

Table 32. Exact weight of mercury, used in no-mix experiment #2 (0.6 mL Hg)

	Weight, g
Syringe initial	2.5211
Syringe with Hg	10.6423
Syringe after	2.5238
Hg injected	8.1185
Hg left in syringe	0.0027

Table 33. Mercury vapour concentration measured by CVAFS; no-mix experiment #2; 0.6 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0.00	0
3	0.05	0.710
7	0.12	1.832
11	0.18	2.696
16	0.27	3.400
22	0.37	3.703
30	0.50	4.303
60	0.99	5.104
100	1.67	5.502
200	3.33	4.304
990	16.42	0.642
1950	32.33	0.320
3500	58.42	0.166
5250	87.50	0.097
9290	154.83	0.022
11580	193.00	0.019
12180	203.00	0.002

Table 34. Mercury vapour concentration measured by AAS; no-mix experiment #2; 0.6 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0	0
0.5	0.008	0.013
1	0.017	0.142
3	0.050	0.736
5	0.083	1.305
10	0.167	2.464
20	0.333	3.708
30	0.500	4.351
60	1	5.154
120	2	5.376
180	3	4.819
300	5	2.920
600	10	1.197
1440	24	0.426
2160	36	0.299
2880	48	0.226
3600	60	0.188
4320	72	0.130
5040	84	0.099
5760	96	0.075
6480	108	0.057
7200	120	0.043

Task 2 experimental raw data: temperature and pressure change in sulphur experiments without mixing

Table 35. Temperature and change of pressure during two experiments (#1 – 0.8 mL Hg and #2 – 0.6 mL Hg)

		No mix experiment #1 - 0.8mL Hg		No mix experiment #2 - 0.6 mL Hg	
Time, min	Time, hr	Temperature, °C	Pressure change, Pa	Temperature, °C	Pressure change, Pa
0	0	21.47	0.00	19.17	0.00
0.5	0.008	21.49	2.43	19.17	0.58
1	0.017	21.98	0.65	19.17	3.45
3	0.050	21.82	3.02	19.17	0.51
5	0.083	21.48	2.63	19.19	0.26
10	0.167	22.02	0.38	19.20	3.68
20	0.333	22.20	0.17	19.37	1.00
30	0.500	21.48	2.93	19.34	0.97
60	1	22.18	2.18	19.33	3.13
120	2	21.88	0.22	19.30	3.83
180	3	19.77	2.76	19.29	1.95
300	5	20.75	0.12	19.24	0.81
600	10	21.19	0.88	19.22	2.58
1440	24	21.48	1.66	19.21	2.52
2160	36	21.36	1.35	19.23	1.87
2880	48	21.16	0.40	19.29	0.93
3600	60	20.88	2.05	19.36	0.46
4320	72	20.73	1.39	19.41	0.62
5040	84	20.63	1.36	19.48	1.89
5760	96	20.52	3.41	19.49	1.64
6480	108	20.41	3.42	19.51	0.91
7200	120	20.36	3.35	19.56	0.50

Task 2 experimental raw data: CVAFS and AAS mercury vapour analysis in sulphur experiments with mixing at 150 rpm

Table 36. Exact weight of mercury, used in mix experiment #1 (1 mL Hg)

	Weight, g
Syringe initial	2.5208
Syringe with Hg	15.9581
Syringe after	2.5344
Hg injected	13.4237
Hg left in syringe	0.0136

Table 37. Mercury vapour concentration measured by CVAFS; mix experiment #1; 1 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0.00	0.000
5	0.08	2.712
10	0.17	5.315
15	0.25	6.602
25	0.42	8.121
40	0.67	9.414
60	1.00	10.025
100	1.67	10.022
120	2.00	9.503
200	3.33	8.302
300	5.00	7.150
500	8.33	5.450
800	13.33	0.392
1004	16.73	0.300
1366	22.77	3.301
1917	31.95	0.201
2924	48.73	0.100
3647	60.78	0.308
4807	80.12	0.570
5182	86.37	0.250
5851	97.52	0.130
6165	102.75	0.550
7570	126.17	0.110

Table 38. Mercury vapour concentration measured by AAS; mix experiment #1; 1 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0	0
0.5	0.008	0.017
1	0.017	0.018
3	0.050	0.765
5	0.083	2.678
10	0.167	5.278
20	0.333	7.414
30	0.500	8.556
60	1	10.145
120	2	9.687
180	3	8.582
300	5	7.089
600	10	0.777
1440	24	1.728
2160	36	0.124
2880	48	0.062
3600	60	0.342
4320	72	0.275
5040	84	0.222
5760	96	0.176
6480	108	0.304
7200	120	0.105

Table 39. Exact weight of mercury, used in mix experiment #2 (0.5 mL Hg)

	Weight, g
Syringe initial	2.5301
Syringe with Hg	9.2982
Syringe after	2.6131
Hg injected	6.6851
Hg left in syringe	0.083

Table 40. Mercury vapour concentration measured by CVAFS; mix experiment #2; 0.5 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0.00	0
7.4	0.12	2.001
16	0.27	3.403
60	1.00	5.017
61	1.02	5.035
101	1.68	5.250
120	2.00	5.201
212	3.53	4.391
840	14.00	1.270
1039	17.32	0.890
1442	24.03	2.015
2765	46.08	0.500
4929	82.15	0.320
6777	112.95	0.300
8978	149.63	0.200

Table 41. Mercury vapour concentration measured by AAS; mix experiment #2; 0.5 mL Hg

Time, min	Time, hr	Hg mg/m^3
0	0	0
0.5	0.008	0.098
1	0.017	0.225
3	0.050	0.812
5	0.083	1.372
10	0.167	2.505
20	0.333	3.709
30	0.500	4.322
60	1	5.079
120	2	5.284
180	3	4.761
300	5	4.714
600	10	2.314
1440	24	2.048
2160	36	0.657
2880	48	0.469
3600	60	0.431
4320	72	0.376
5040	84	0.382
5760	96	0.358
6480	108	0.352
7200	120	0.285

Task 2 experimental raw data: temperature and pressure change in sulphur experiments with mixing at 150 rpm

Table 42. Temperature and change of pressure during two sulphur experiments (#1 – 1 mL Hg @ 150 rpm and #2 – 0.5 mL Hg @ 150 rpm)

		Experiment with mixing #1 - 1 mL Hg		Experiment with mixing #2 -0.5 mL Hg	
Time, min	Time, hr	Temperature, °C	Pressure change, Pa	Temperature, °C	Pressure change, Pa
0	0	19.92	0.00	20.31	0.00
0.5	0.008	19.91	0.83	20.31	1.90
1	0.017	19.90	1.33	20.31	3.33
3	0.050	19.89	0.44	20.30	2.61
5	0.083	19.88	0.54	19.93	1.05
10	0.167	19.88	1.13	20.30	3.31
20	0.333	19.60	1.37	19.95	2.64
30	0.500	19.49	3.61	20.24	2.96
60	1	19.35	1.91	19.97	0.15
120	2	19.52	2.64	20.44	2.23
180	3	19.82	3.19	20.20	3.03
300	5	19.98	1.26	20.11	0.63
600	10	20.00	1.14	20.43	2.21
1440	24	19.84	3.76	20.24	2.96
2160	36	19.59	2.89	20.40	2.61
2880	48	19.49	2.53	20.10	1.15
3600	60	20.04	3.64	19.99	0.85
4320	72	20.26	0.24	20.31	0.81
5040	84	19.47	2.47	20.49	1.16
5760	96	20.04	1.95	20.31	0.84
6480	108	19.84	2.34	20.28	0.20
7200	120	19.59	1.52	20.11	1.41

Task 3.

Diphenylcarbazide spectrophotometric method of mercuric ion analysis validation raw data

Indicator: mixture 2:1 diphenylcarbazone and diphenylcarbazide.

Table 43. Method calibration and validation data

μL	mL	μL	mL	$[Hg^{+2}]$	560 nm
STD 1% $Hg(Ac)_2$	DMFA	V mix	DPK	mg/L	Abs. A
50	3	0	3	0	0
50	3	10	3	16.88	0.085
50	3	20	3	33.66	0.179
50	3	30	3	50.32	0.255
50	3	40	3	66.87	0.333
50	3	50	3	83.31	0.4
50	3	60	3	99.65	0.477
50	3	70	3	115.9	0.54
50	3	80	3	132	0.615
50	3	90	3	148	0.674
50	3	100	3	163.9	0.73
50	3	110	3	179.7	0.79
50	3	120	3	195.5	0.84
50	3	130	3	211.1	0.89
50	3	140	3	226.6	0.945
50	3	150	3	242	0.992
50	3	160	3	257.3	1.044
50	3	170	3	272.5	1.085
50	3	180	3	287.7	1.133
50	3	190	3	302.7	1.165
50	3	200	3	317.6	1.205
50	3	210	3	332.5	1.252
50	3	220	3	347.2	1.278
50	3	230	3	361.9	1.314
50	3	240	3	376.4	1.352
50	3	250	3	390.9	1.384
50	3	260	3	405.3	1.409
50	3	270	3	419.6	1.435
50	3	280	3	433.8	1.472
50	3	290	3	448	1.507
50	3	300	3	462	1.535
50	3	310	3	476	1.549
50	3	320	3	489.8	1.579
50	3	330	3	503.6	1.601
50	3	340	3	517.3	1.607
50	3	350	3	531	1.635
50	3	360	3	544.5	1.65
50	3	370	3	558	1.67

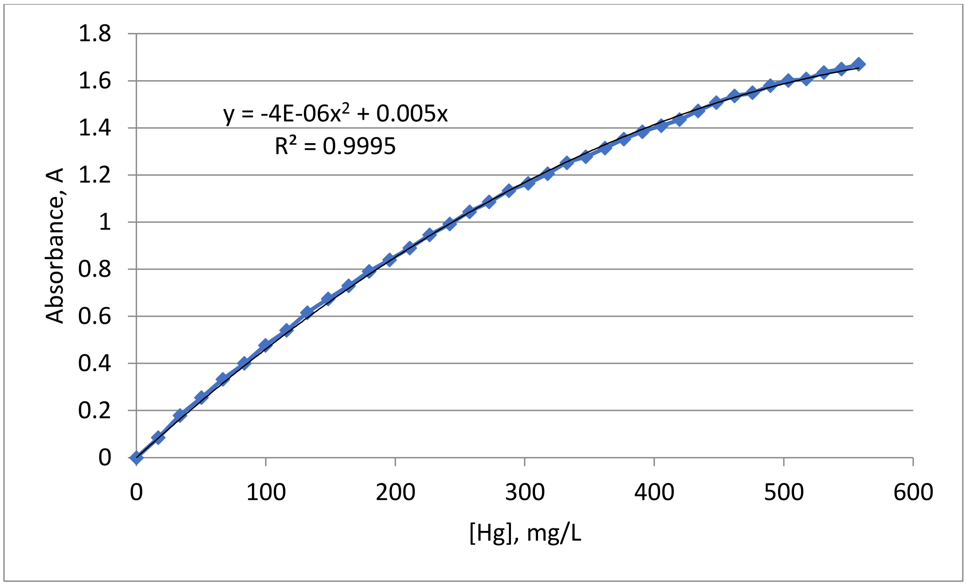

Figure 40. Diphenylcarbazide spectrophotometric method calibration and validation data plot

Diphenylcarbazide spectrophotometric method validation results:

Range is 0.3 – 600 mg/mL $Hg(Ac)_2$ (0.05 – 100% conversion)

Lower Limit of Quantitation is 0.3 mg/mL $Hg(Ac)_2$

Limit of Detection is 0.1 mg/mL $Hg(Ac)_2$

Linearity (quadratic) r^2 is 0.9995

Task 3 experimental raw data: Yield of reaction of mercury with vinegar (0 – 60 min) and with vinegar – hydrogen peroxide mixture (60 – 120 min) measured by mercuric acetate and by mercury without mixing and with mixing at 150 rpm

Yield measured by diphenylcarbazide spectrophotometric method referred as “By $Hg(Ac)_2$”

Yield measured by gravimetric method (II) referred as “By Hg^0”

Table 44.Yield of reaction by mercuric acetate and by mercury without mixing, in %

	Experiment #1		Experiment #2	
Time, min	By $Hg(Ac)_2$, %	By Hg^0, %	By $Hg(Ac)_2$, %	By Hg^0, %
0	0	0	0	0
5	0	0	0	0
10	0	0	0	0
30	0	0	0	0
60	0	0	0	0
65	0.086	0.090	0.071	0.090
70	0.166	0.175	0.155	0.146
90	0.471	0.535	0.511	0.500
120	0.925	0.945	0.990	1.062

Table 45.Yield of reaction by mercuric acetate and by mercury with mixing at 150 rpm, in %

	Experiment #1		Experiment #2	
Time, min	By $Hg(Ac)_2$, %	By Hg^0, %	By $Hg(Ac)_2$, %	By Hg^0, %
0	0.000	0.000	0.000	0.000
5	0.000	0.000	0.000	0.000
10	0.000	0.000	0.000	0.000
30	0.000	0.000	0.000	0.000
60	0.000	0.000	0.000	0.000
65	0.083	0.079	0.110	0.112
70	0.200	0.225	0.236	0.257
90	0.715	0.700	0.776	0.802
120	1.579	1.554	1.688	1.633

Task 3 experimental raw data: CVAFS and AAS analysis of mercury vapour produced by liquid mercury treated with vinegar and vinegar – hydrogen peroxide mixture without mixing

Table 46. Mercury vapour concentration measured by CVAFS; no-mix experiment #1

Time, min	Hg mg/m^3
0	0
5	0.055
10	0.079
15	0.109
20	0.127
30	0.190
40	0.222
55	0.268
65	1.206
70	2.000
80	2.505
100	3.304
120	3.452

Table 47. Mercury vapour concentration measured by AAS; no-mix experiment #1

Time, min	Hg mg/m^3
0	0.000
5	0.053
10	0.085
20	0.125
30	0.157
40	0.177
58	0.207
60	0.207
62	0.642
65	1.351
67	1.624
70	1.828
75	2.396
80	2.600
85	2.737
90	2.817
95	3.121
100	3.219
110	3.328
120	3.407

Table 48. Mercury vapour concentration measured by CVAFS; no-mix experiment #2

Time, min	Hg mg/m^3
0	0
7	0.061
10	0.076
17	0.105
22	0.129
27	0.159
45	0.206
58	0.233
65	1.504
75	2.300
90	2.907
100	3.456
120	3.559

Table 49. Mercury vapour concentration measured by AAS; no-mix experiment #2

Time, min	Hg mg/m^3
0	0.000
5	0.060
10	0.071
20	0.105
30	0.159
40	0.183
58	0.204
60	0.201
62	0.854
65	1.409
67	1.657
70	1.908
75	2.505
80	2.707
85	2.808
90	2.856
95	3.205
100	3.355
110	3.457
120	3.486

Task 3 experimental raw data: temperature and pressure change produced by liquid mercury treated with vinegar and vinegar – hydrogen peroxide mixture without mixing

Table 50. Temperature and pressure change in experiments #1 and #2 without mixing

	Experiment #1, no mix		Experiment #2, no mix	
Time, min	Temperature, °C	Pressure change, Pa	Temperature, °C	Pressure change, Pa
0	19.80	0.00	20.27	0.00
5	19.80	4.70	20.33	1.22
10	19.79	1.15	20.27	2.16
20	19.81	2.72	20.27	3.56
30	19.79	4.49	20.26	1.55
40	19.78	8.11	20.26	4.22
58	19.77	2.86	20.32	5.46
60	19.80	4.56	20.30	5.24
62	19.79	6.29	20.32	7.03
65	20.02	16.11	20.48	12.46
67	20.01	21.65	20.56	23.57
70	20.00	27.92	20.45	25.65
75	19.99	26.99	20.50	37.13
80	19.97	48.69	20.50	59.33
85	19.97	63.92	20.52	59.33
90	19.96	83.04	20.50	75.14
95	19.94	76.17	20.43	85.33
100	19.89	89.76	20.41	86.33
110	19.93	111.62	20.48	126.26
120	19.91	150.47	20.44	141.25

Task 3 experimental raw data: CVAFS and AAS analysis of mercury vapour produced by liquid mercury treated with vinegar and vinegar – hydrogen peroxide mixture with mixing at 150 rpm

Table 51. Mercury vapour concentration measured by CVAFS; experiment with mixing at 150 rpm #1

Time, min	Hg mg/m^3
0	0
7	0.257
10	0.360
18	0.408
25	0.559
35	0.678
42	0.744
60	1.010
67	4.002
74	4.209
82	4.107
110	4.000
125	3.981

Table 52. Mercury vapour concentration measured by AAS; experiment with mixing at 150 rpm #1

Time, min	Hg mg/m^3
0	0.000
5	0.182
10	0.269
20	0.425
30	0.589
40	0.714
58	0.950
60	0.982
62	1.735
65	4.156
67	4.180
70	4.163
75	4.014
80	3.909
85	3.887
90	3.892
95	3.903
100	3.925
110	3.930
120	3.933

Table 53. Mercury vapour concentration measured by CVAFS; experiment with mixing at 150 rpm #2

Time, min	Hg mg/m^3
0	0
7	0.108
12	0.201
18	0.305
28	0.402
35	0.501
42	0.602
55	0.750
67	3.707
74	3.909
82	3.957
100	4.003
120	4.059

Table 54. Mercury vapour concentration measured by AAS; experiment with mixing at 150 rpm #2

Time, min	Hg mg/m^3
0	0.000
5	0.100
10	0.188
20	0.330
30	0.459
40	0.562
58	0.751
60	0.853
62	1.204
65	3.508
67	3.802
70	3.953
75	4.006
80	4.029
85	4.005
90	3.982
95	3.959
100	3.941
110	3.920
120	3.906

Task 3 experimental raw data: temperature and pressure change produced by liquid mercury treated with vinegar and vinegar – hydrogen peroxide mixture with mixing at 150 rpm

Table 55. Temperature and pressure change in experiments #1 and #2 with mixing at 150 rpm

	Experiment #1, mix		Experiment #2, mix	
Time, min	Temperature, °C	Pressure change, Pa	Temperature, °C	Pressure change, Pa
0	20.17	0.00	20.53	0.00
5	20.01	4.49	20.50	-2.10
10	20.03	10.83	20.43	5.13
20	20.02	11.24	20.59	0.26
30	20.08	4.90	20.26	10.15
40	20.03	-3.08	20.42	6.33
58	20.16	-1.45	20.56	3.13
60	20.14	0.40	20.26	5.13
62	20.17	7.58	20.51	19.24
65	20.28	35.13	20.63	20.32
67	20.26	22.46	20.69	41.24
70	20.34	33.03	20.69	38.13
75	20.38	63.87	20.61	50.13
80	20.25	70.37	20.60	75.12
85	20.27	90.98	20.42	102.13
90	20.24	113.44	20.39	110.33
95	20.18	137.53	20.67	124.36
100	20.20	151.39	20.40	164.55
110	20.16	194.67	20.51	208.36
120	20.19	238.14	20.37	262.14

Table 56. Estimation of volume of released oxygen

$P_1V_1 = P_2V_2$	mixed		not mixed	
Atmospheric pressure	101325.00	Pa	101325.00	Pa
Max. differential pressure	270.00	Pa	160.00	Pa
Absolut max. pressure	101595.00	Pa	101485.00	Pa
Actual volume of the reactor	3596.00	mL	3596.00	mL
Increased total volume	3605.58	mL	3601.68	mL
Volume of oxygen	**9.58**	**mL**	**5.68**	**mL**