Green and Sustainable Chemistry, 2024, 14, 29-41
https://www.scirp.org/journal/gsc
ISSN Online: 2160-696X
ISSN Print: 2160-6951

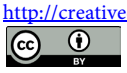
Calibration of CO and CO_2 Monitors Used in Periodic Inspection of Vehicles at Fixed Stations for Environmental Control

Adel Bassuoni Shehata*, Abdulrahman Rashed Al Askar, Najjy Hamad Al Yami, Abdullah Suleiman Al Owaysi, Sultan K. Alharbi

Chemistry Department, National Measurement and Calibration Center (NMCC), Saudi Standards, Metrology and Quality Organization (SASO), Riyadh, Kingdom of Saudi Arabia
Email: *adelshehata63@yahoo.com

How to cite this paper: Shehata, A.B., Al Askar, A.R., Al Yami, N.H., Al Owaysi, A.S. and Alharbi, S.K. (2024) Calibration of CO and CO_2 Monitors Used in Periodic Inspection of Vehicles at Fixed Stations for Environmental Control. *Green and Sustainable Chemistry*, **14**, 29-41.
https://doi.org/10.4236/gsc.2024.142003

Received: April 21, 2024
Accepted: May 25, 2024
Published: May 28, 2024



Abstract

Global efforts for environmental cleanliness through the control of gaseous emissions from vehicles are gaining momentum and attracting increasing attention. Calibration plays a crucial role in these efforts by ensuring the quantitative assessment of emissions for informed decisions on environmental treatments. This paper describes a method for the calibration of CO/CO_2 monitors used for periodic inspections of vehicles in cites. The calibration was performed in the selected ranges: 900 - 12,000 µmol/mol for CO and 2000 - 20,000 µmol/mol for CO_2. The traceability of the measurement results to the SI units was ensured by using certified reference materials from CO/N_2 and CO_2/N_2 primary gas mixtures. The method performance was evaluated by assessing its linearity, accuracy, precision, bias, and uncertainty of the calibration results. The calibration data exhibited a strong linear trend with R^2 values close to 1, indicating an excellent fit between the measured values and the calibration lines. Precision, expressed as relative standard deviation *(%RSD),* ranged from 0.48 to 4.56% for CO and from 0.97 to 3.53% for CO_2, staying well below the 5% threshold for reporting results at a 95% confidence level. Accuracy measured as percent recovery, was consistently high (≥ 99.1%) for CO and ranged from 84.90% to 101.54% across the calibration range for CO_2. In addition, the method exhibited minimal bias for both CO and CO_2 calibrations and thus provided a reliable and accurate approach for calibrating CO/CO_2 monitors used in vehicle inspections. Thus, it ensures the effectiveness of exhaust emission control for better environment.

Keywords

Monitors, Periodic Inspection, CO/CO_2 Calibration, Linearity, Precision, Accuracy

1. Introduction

The monitoring of carbon monoxide (CO) and carbon dioxide (CO_2) in car exhaust emissions plays a crucial role in regulating air quality and ensuring adherence to environmental standards [1] [2]. Monitoring is also important for health reasons since vehicle emissions result in environmental pollution causing cardiovascular and lung diseases [3] [4] [5] [6] [7]. The amount of CO, CO_2, NOx and hydrocarbon emissions produced by old cars is seven times higher than that of new vehicles. Therefore, periodical vehicle emission checks are crucial for environmental control [8]. Monitoring of vehicles emissions is carried out in toll stations, because they include traffic congestion, idling vehicles, and frequent acceleration, which leads to significant increases in emissions causing environmental problems [9] [10]. To assess the severity of this pollution, fixed monitoring stations are often positioned near toll collection points [11]. In recent years, mobile monitoring of vehicle emissions has also gained significant attraction among researchers, since it offers real-time, on-the-go detection of pollutants directly from moving vehicles. Portable Emission Measurement Systems (PEMS) stand out as a particularly reliable method within mobile monitoring [12] [13] [14]. In addition, periodic motor vehicles inspection is carried out at fixed stations equipped with CO, CO_2 and HC monitors. The quality of emission data depends on the condition of the monitor, which can be noticed from its response values to the CRM mole fractions. It also depends on the reliability and validity of the CRM used for calibration. The measured gaseous emission values are then compared to the permissible limits established by the regulations in force within countries that utilize this approach and inspected cars are either licensed or rejected accordingly like in Saudi Arabia [15]. However, the validity of these measurements depends on the accuracy and reliability of the monitoring instruments, which is attained by calibration using certified reference materials (CRMs) to ensure traceability to the SI units. Metrological traceability is defined as: property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty [16]. In the present paper, we describe the development and validation of a calibration method for carbon monoxide (CO) and carbon dioxide (CO_2) monitors used in periodic inspections of vehicles at fixed stations in Saudi Arabia. The proposed method utilizes CO and CO_2 primary gas mixtures CRMs to ensure traceability of the measurement results to the SI units. The linearity, precision, accuracy and bias of the calibration method will be studied to establish its performance characteristics [17]. Additionally, an uncertainty budget will be assessed to quantify the various sources of uncertainty associated with the calibration results [18]. This developed calibration method will enhance the reliability of data collected from motor vehicles periodic inspection networks leading to more accurate vehicles inspection and improved environmental decision making.

2. Materials and Methods

2.1. Equipment

The exhaust gas monitor utilized in stations of periodic technical inspection of vehicles for measuring CO and CO_2 exhaust levels was of model CET 210, manufactured by CARTEC, Italy. This monitor requires a 10 min warm-up time and operates with a gas flow of 4 L/min, with a minimum acceptable flow of 2.5 L/min. In addition, it features an rpm counter ranging from 300 to 9990 /min, a power supply of 11/15 V DC, and a pressure range of 85 - 106 kPa.

2.2. The CO and CO_2 CRMs

Two series of CO/N_2 and CO_2/N_2 primary gas mixtures were produced at SASO/NMCC as certified reference materials in accordance with the requirements of ISO 6142, ISO 6143 and ISO 17034 using the same procedure published before for CO and CO_2 monitors calibration [19] [20] [21]. Each CRM series contains 5 ascending mole fractions with associated expanded uncertainty as shown in Table 1.

Table 1. The CO and CO_2 CRMs used for calibration of exhaust monitors.

CO/N_2					
Cylinder code	**PSM266484**	**PSM266396**	**PSM266443**	**PSM298348**	**PSM266458**
Mole fraction (μmol/mol)	988.875	2493.118	6810.028	8196.32	11482.979
U_{exp} (μmol/mol)	1.15	6.14	7.01	5.15	7.3
CO_2/N_2					
Cylinder code	**PSM298317**	**PSM266408**	**PSM266479**	**PSM298259**	**PSM266486**
Mole fraction (μmol/mol)	2497.000	4893.039	12249.490	16151.317	19965.534
U_{exp} (μmol/mol)	2.5	4.55	4.91	5.22	7.21

These CRMs were filled-in in 5 L aluminum cylinders supplied from Air Liquide (Netherlands). A gas cylinder regulator (CONCOA, USA) was used to control the gas flow from each cylinder. The high-purity nitrogen gas (99.999%) used to establish the zero background before calibration was obtained from LINDE-SIGAS (Germany).

2.3. Calibration Procedures

Calibration was performed for a monitor that reads CO and CO_2 at a station in the city of Jeddah. The resolution of the monitor was 0.01 and the accuracy was 0.2%. In the calibration process, the five CRM cylinders were measured in an ascending order stating from the smallest mole fraction up to the largest one. The calibration procedure begins by powering on the monitor then connecting

the nitrogen gas cylinder to it using a regulator and a plastic pipeline to establish the zero background. When the zero-reading appeared and remained stable for one minute, the nitrogen cylinder was disconnected and the first CO or CO_2 CRM cylinder was connected to the monitor at the safe pressure specified in the manual. The CO or CO_2 mole fraction was measured five times, taking one measurement per minute, and the calibration results were recorded. Once finished with the first cylinder, it was disconnected and we proceeded to the next one until the five CRM cylinders were measured (see Figure 1). The response of the monitors in % was converted to μmol/mol (ppm) in order to interpret the results in terms of SI units.

Figure 1. Calibration of CO/CO_2 monitors using CRMs.

3. Results and Discussion

3.1. The Calibration Lines

Accurate exhaust CO and CO_2 measurement results are ensured by calibrating the measuring monitors using certified reference materials (CRMs). The calibration range was chosen based on customer request: 900 - 12,000 ppm for CO and 2000 - 20,000 ppm for CO_2. Figure 2 presents the calibration results for the CO monitor. As shown by the equation, $y = 0.9987x - 10.359$, the calibration data follows a linear trend. The R^2 value of unity signifies an excellent fit between the data points and the calibration line [2]. The slope of the calibration line (0.9987), which is near unity, indicates high sensitivity of the monitor since the sensor output response is almost identical to a unit change in the CO CRM mole fraction. This linear relationship between the CRM CO mole fraction and the monitor response, along with the high R^2 value, confirms that the CO monitor is functioning properly within the CO mole fraction range tested during calibration.

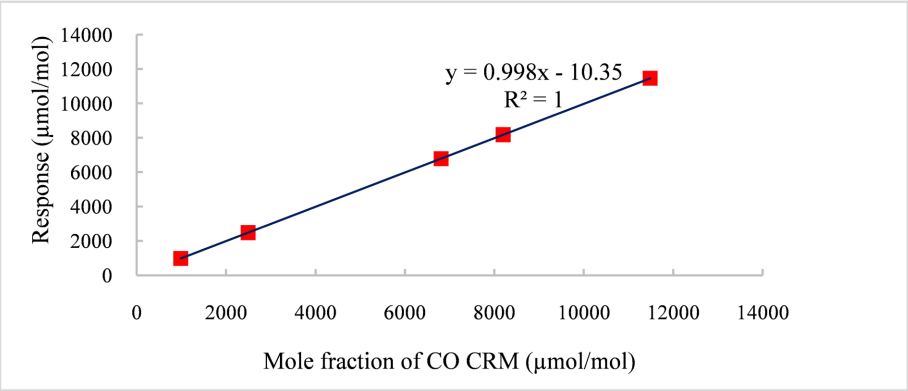


Figure 2. Calibration graph of CO monitor.

Examining **Figure 3**, the calibration curve for the CO_2 monitor also shows goo linearity, expressed by the equation y = 1.0227x − 332.17. The R^2 value (0.9992), close to 1, indicates a good fit of the measured points to the line. Similar to the CO monitor, the slope approaching 1 suggests high monitor sensitivity.

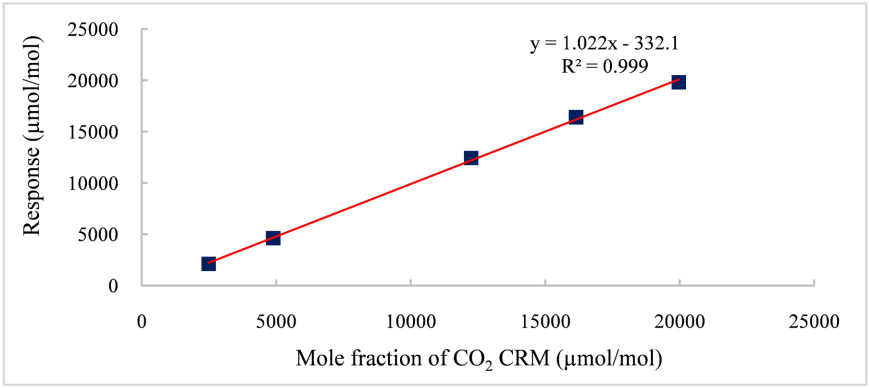


Figure 3. Calibration graph of CO_2 monitor.

3.2. Precision

According to ICH, the precision of an analytical procedure is usually expressed as the variance, standard deviation, or coefficient of variation of a series of measurements [22]. The coefficient of variation (%RSD) calculated by equation 1 is a unitless value, which allows for easier comparison between calibration results.

$$\%RSD = \frac{SD}{\bar{x}} \times 100 \quad (1)$$

The %RSD threshold of 5% is often considered the limit of acceptable precision when reporting the results at a 95% confidence interval. A lower %RSD indicates a more precise calibration result, and vice versa. Looking at the results of the CO calibration in **Table 2**, we find that all the CO response levels produced consistent standard deviations and %RSD ranging from 0.48 to 4.56%, which indicates quite satisfactory precision. In the case of the CO_2 monitor calibration

results, we find that the standard deviation fell into two categories: the first is (44.72, 44.72) and the second is (438.18, 447.21, 447.21). This difference can be attributed to the inherently less stable nature of CO_2 measurements compared to CO. Nevertheless, the corresponding %RSD ranged from 0.97 to 3.53%, which were consistent and lower than 5%, ensuring good precision of the calibration method as well.

Table 2. The calibration results of CO and CO_2 exhaust monitors.

	CO Monitor				
Monitor response (µmol/mol)	900	2400	6700	8100	11400
	1000	2500	6800	8200	11400
	1000	2500	6800	8200	11500
	1000	2500	6800	8200	11500
	1000	2500	6800	8200	11500
$\bar{x}$	980	2480	6780	8180	11460
SD	44.72	44.72	44.72	44.72	54.77
%RSD	4.56	1.80	0.66	0.55	0.48
	CO_2 Monitor				
Monitor response (µmol/mol)	2200	4700	13200	17200	19000
	2100	4600	12200	16200	20000
	2100	4600	12300	16200	20000
	2100	4600	12200	16200	20000
	2100	4600	12200	16200	20000
$\bar{x}$	2120	4620	12420	16400	19800
SD	44.72	44.72	438.18	447.21	447.21
%RSD	2.11	0.97	3.53	2.73	2.26

3.3. Accuracy (Recovery)

Table 3 shows recovery results for CO and CO_2 calibration results. Recovery was calculated using equation 2 and it refers to the percentage of the average ($\bar{x}$) concentration of a certified reference material (CRM) [17].

$$R(\%) = \frac{\bar{x}}{x_{CRM}} \times 100 \tag{2}$$

Table 3. The recovery (accuracy) results of the CO and CO_2 calibrations.

			CO Monitor		
CRM (µmol/mol)	988.88	2493.12	6810.03	8196.32	11482.98
$\bar{x}$ (µmol/mol)	980	2480	6780	8180	11460
% Recovery	99.10	99.47	99.56	99.80	99.80
			CO_2 Monitor		
CRM (µmol/mol)	2497.00	4893.04	12249.49	16151.32	19965.53
$\bar{x}$ (µmol/mol)	2120	4620	12420	16400	19800
% Recovery	84.90	94.42	101.39	101.54	99.17

Form this table, the CO % recovery values are very high (99.10% to 99.80%), indicating the method is accurately measuring CO mole fraction. There is a slight upward trend in recovery with increasing CRM mole fraction, though the difference is minimal. With regard to the CO_2, the % recovery, was more variable (84.90% to 101.54%), suggesting the method might be affected by CO_2 mole fraction. Three recoveries exceed 100%, possibly due to matrix effects *i.e.* other compounds influencing the CO_2 measurement. Overall, recoveries indicate that the method seems very reliable and accurate for CO and CO_2 calibration results.

3.4. Bias

In calibration methods, bias which is a systematic error causing consistent deviation from the true value, is identified by comparing instrument readings to a known CRM value, and understanding this discrepancy is crucial for accurate measurements and informed decisions based on reliable data. The absolute and % bias in the CO and CO_2 calibration results were calculated by equations 3 and 4 and reported in **Table 4** [17].

$$b = \bar{x} - x_{CRM} \tag{3}$$

$$b(\%) = \frac{\bar{x} - x_{CRM}}{x_{CRM}} \times 100 \tag{4}$$

Table 4. Results of evaluation of the CO and CO_2 calibration method bias.

	CO Monitor				
u_{Rept} $(SD/\sqrt{n})$	20.00	20.00	20.00	20.00	24.49
σ	20.03	20.92	21.19	20.65	25.56
$+2\sigma$	40.07	41.84	42.39	41.30	51.12
-2σ	−40.07	−41.84	−42.39	−41.30	−51.12
bias (μmol/mol)	−8.88	−13.12	−30.03	−16.32	−22.98
bias %	−0.90	−0.53	−0.44	−0.20	−0.20
	CO_2 Monitor				
u_{Rept} $(SD/\sqrt{n})$	20.00	20.00	195.96	200.00	200.00
σ	20.16	20.51	196.02	200.07	200.13
$+2\sigma$	40.31	41.02	392.04	400.14	400.26
-2σ	−40.31	−41.02	−392.04	−400.14	−400.26
bias (μmol/mol) (μmol/mol)	−377.00	−273.04	170.51	248.68	−165.53
bias %	−15.10	−5.58	1.39	1.54	−0.83

To assess the significance of the bias, equation 5 was used, where the standard deviation (σ) was calculated by equation 6, combining the squared repeatability uncertainty and the standard uncertainty of the CRM [23] [24]. The calculated σ was reported in **Table 4** with values of the −2 σ and +2 σ.

$$-2\sigma \le b \le +2\sigma \tag{5}$$

$$\sigma = \sqrt{\left(\frac{SD}{\sqrt{n}}\right)^2 + (u_{CRM})^2} \tag{6}$$

From this table, it can be seen that, in case of the five CO calibration levels, the

bias values were inside the expected range of variation, $-2\sigma \leq b \leq +2\sigma$. This means that no statistically significant bias was found. With regard to the CO_2 calibration, level 1 exhibited a bias of −377 μmol/mol, which was less than -2σ (−40.31 μmol/mol). Likewise, level 2 exhibited a bias of −273.04 μmol/mol which was less than -2σ (−41.02 μmol/mol). Meanwhile, the bias values of calibration levels 3, 4, and 5 were smaller than $+2\sigma$. This means that bias of the CO_2 calibration levels 1, 2, 3, 4 and 5 fall inside the range of $-2\sigma \leq b \leq +2\sigma$. Hence, no statistically significant bias was found in the CO and CO_2 calibration method results, which, increases confidence in the accuracy of the measurements made using that method.

3.5. The Uncertainty of Measurements

Estimating the uncertainty associated with calibration results of CO and CO_2 exhaust monitors is crucial for ensuring the reliability of the measured gas mole fractions. The measurand is the mole fraction (y) of the CO and CO_2 gas emissions that is defined in equation 7 and the uncertainty estimation was based on ISO GUM [25].

$$y = a\,x + b \tag{7}$$

where,

y—response of the monitor;

x—mole fraction of CRM (μmol/mol);

b—intercept;

a—slope.

From this equation, the explicit sources of uncertainty are: 1) slope, 2) mole fraction of the CRM (x) and 3) the intercept. Beyond these explicit sources, additional implicit uncertainties are: 1) monitor resolution, 2) monitor accuracy and 3) repeatability of the monitor response.

3.5.1. Estimation of Uncertainty of Explicit Sources

The standard uncertainty of the CRM mole fraction was calculated by dividing the expanded uncertainty, U_{exp} laid down in the CRM certificate by 2 using equation 8.

$$u_{CRM} = \frac{U_{\exp}}{2} \tag{8}$$

With regard to the uncertainty of the slope and intercept, it is required firstly to determine the standard deviation of the residuals, S using equation 9.

$$S = \sqrt{\frac{\sum_{i=1}^{N}\left(y_i - b - ax_i\right)^2}{N-2}} \tag{9}$$

where,

N—is the number of measurements in the calibration process;

y—is the response of the monitor;

b—is the intercept;

a—is the slope;

x—is the mole fraction of CRM.

Using the calculated S value, the uncertainty of the slope, *u(a)* was calculated by equation 10

$$u(a) = \sqrt{\frac{S^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}} \tag{10}$$

where,

S—standard deviation of regression;

x_i—is the mole fraction of the CRM;

$\bar{x}$ —is the average mole fraction of CRM.

The uncertainty of the intercept was calculated using equation 11.

$$u(b) = \sqrt{\frac{S^2 \sum_{i=1}^{n} x_i^2}{n\sum_{i=1}^{n}(x_i - \bar{x})^2}} \tag{11}$$

3.5.2. Estimation of Uncertainty of Implicit Sources

The resolution and accuracy are two technical specifications of the CO/CO_2 monitorsand their uncertainty contributions were determined by equations 12 and 13 respectively.

$$u_{resol} = \frac{Resolution}{2\sqrt{3}} \tag{12}$$

$$u_{Accu} = \frac{\%Accu}{\sqrt{3}} \cdot \bar{x} \tag{13}$$

The uncertainty (Type A) of the repeatability of the monitor response was calculated by equation 14, in which *SD* is the standard deviation and *n* is the number of measurements.

$$u_{rept} = \frac{SD}{\sqrt{n}} \tag{14}$$

In order to fit the three implicit sources of uncertainty into the mathematical model, they were denoted by the term δz and combined by equation 15 in which c_1, c_2 and c_3 are the sensitivity coefficients [26]. Each of these coefficients equals 1 since the three uncertainties were expressed in μmol/mol like CO and CO_2 gases [27].

$$\partial z = \sqrt{(c_1 \cdot u_{resol})^2 + (c_2 \cdot u_{accu})^2 + (c_3 \cdot u_{rept})^2} \tag{15}$$

The mathematical model in equation 7 was then modified in equation 16 by adding the term δz in condition that its mole fraction equals zero but it contributes to the uncertainty associated with the measured mole fraction.

$$y = a\,x + b + \partial z \tag{16}$$

Equation 16 was differentiated to determine the sensitivity coefficients, which account for how each source of uncertainty influences the final mole fraction measurement. The combined standard uncertainty, u_c was calculated by equa-

tion 17 in which $\delta y/\delta a$, $\delta y/\delta x$, $\delta y/\delta b$ and $\delta y/\delta z$ are the sensitivity coefficients of the slope, mole fraction of the CRM, intercept and the term δz respectively.

$$u_c = \sqrt{\left(\frac{\partial y}{\partial a}\cdot u_a\right)^2 + \left(\frac{\partial y}{\partial x}\cdot u_x\right)^2 + \left(\frac{\partial y}{\partial b}\cdot u_b\right)^2 + \left(\frac{\partial y}{\partial z}\cdot u_{\partial z}\right)^2} \quad (17)$$

The expanded uncertainty (U_{exp}) was then calculated using Equation 18 at a confidence level, typically 95% using a coverage factor $k = 2$, and the results were given in Table 5. This uncertainty provides a broader range within which the true value is expected to fall with a specific level of confidence.

$$U_{\exp} = u_c \times k \quad (18)$$

Table 5. The uncertainty budget of CO and CO_2 calibration results.

CO	$\bar{x}$	(μmol/mol)	980	2480	6780	8180	11460
		% U_{exp}	4.23	1.99	1.23	1.17	1.15
CO_2	$\bar{x}$	(μmol/mol)	2120	4620	12420	16400	19800
		% U_{exp}	4.79	4.05	4.85	4.41	4.27

From these results, one can notice that the percent uncertainties for CO calibrations range from 1.15% to 4.23%, with a generally decreasing trend as the mole fraction increases. This suggests that the calibration becomes more precise at higher mole fraction. Meanwhile, the percent uncertainties for CO_2 calibrations range from 4.05% to 4.79%, with no apparent trend across the mole fraction range. This indicates that the calibration uncertainty is independent of the mole fraction for CO_2.

4. Conclusion

A method for the calibration of CO/CO_2 monitors employed in periodic vehicle inspections was developed and assessed. The method demonstrated excellent performance across the chosen calibration ranges with ensured traceability of the measurements to the SI units through certified reference materials. Statistical analysis of the calibration results revealed strong linearity with R^2 almost equals one, high precision (%RSD < 5%) and good accuracy (≥ 99.1% for CO and 84.90% - 101.54% for CO_2). The method also showed a non-significant bias indicating reliable calibration results. Thus, it provides an effective means for exhaust emission control contributing to improved environmental cleanliness in urban centers and supporting global efforts in this critical area.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Shahariar, G.M.H., Mojibul, S., Kabir A.S., Jahirul, M.I., Thuy, C., Zoran, R., Richard, J.B. and Timothy, A.B. (2022) On-Road CO_2 and NO_x Emissions of a Diesel

Vehicle in Urban Traffic. *Transportation Research Part D*: *Transport and Environment*, **107**, Article ID: 103326.
https://www.sciencedirect.com/science/article/abs/pii/S1361920922001547
https://doi.org/10.1016/j.trd.2022.103326

[2] Marek, B. and Paulina, B. (2019) Predicting the Spatial Distribution of Emissions from Urban Buses Based on Previously Measured Data and Scenarios for Their Modernization in the Future. Case Study: Krakow, Poland. *Atmospheric Environment*, **199**, 1-14.
https://www.sciencedirect.com/science/article/pii/S1352231018307751
https://doi.org/10.1016/j.atmosenv.2018.11.009

[3] Wang, J., Wu, Q., Liu, J., Yang, H., Yin, M., Chen, S., Guo, P., Ren, J., Luo, X., Linghu, W. and Huang, Q. (2019) Vehicle Emission and Atmospheric Pollution in China: Problems, Progress, and Prospects. *PeerJ*, **7**, e6932.
https://doi.org/10.7717/peerj.6932

[4] Samoli, E., Atkinson, R.W., Analitis, A., Fuller, G.W., Green, D.C., Mudway, I., Anderson, H.R. and Kelly, F.J. (2016) Associations of Short-Term Exposure to Traffic-Related Air Pollution with Cardiovascular and Respiratory Hospital Admissions in London, UK. *Occupational and Environmental Medicine*, **73**, 300-307.
https://oem.bmj.com/content/73/5/300
https://doi.org/10.1136/oemed-2015-103136

[5] Philip, C., Aonghus, O.D., Margaret, O.M., Anne, N., Frank, M., Brian, B., Martina, H., Aoife, D., Owen, N. and Sean, L. (2021) Local NO_2 Concentrations and Asthma among over-50s in Ireland: A Microdata Analysis. *International Journal of Epidemiology*, **49**, 1899-1908.https://pubmed.ncbi.nlm.nih.gov/32474589/
https://doi.org/10.1093/ije/dyaa074

[6] Geng, L., Shida, S., Chao, Z., Bo, W., Lin, W. and Hongjun, M. (2022) Air Pollutant Emissions from On-Road Vehicles and Their Control in Inner Mongolia, China. *Energy*, **1**, Article ID: 121724.
https://www.sciencedirect.com/science/article/abs/pii/S0360544221019721
https://doi.org/10.1016/j.energy.2021.121724

[7] Strak, M., Janssen, N., Beelen, R., Schmitz, O., Vaartjes, I., Karssenberg, D., van den Brink, C., Bots, M.L., Dijst, M., Brunekreef, B. and Hoek, G. (2017) Long-Term Exposure to Particulate Matter, NO_2 and the Oxidative Potential of Particulates and Diabetes Prevalence in a Large National Health Survey. *Environment International*, **108**, 228-236.
https://www.sciencedirect.com/science/article/pii/S016041201730452X
https://doi.org/10.1016/j.envint.2017.08.017

[8] Hung, L.C., Jiun, H. T., Yung, C. Y. and Ho, W.Y. (2008) Deterioration of Gasoline Vehicle Emissions and Effectiveness of Tune-Up for High-Polluted Vehicles. *Transportation Research Part D*: *Transport and Environment*, **13**, 47-53.
https://www.sciencedirect.com/science/article/abs/pii/S1361920907000879#
https://doi.org/10.1016/j.trd.2007.07.004

[9] Ghadikolaei, M.A., Wei, L., Cheung, C.S. and Yung, K.F. (2019) Effects of Engine Load and Biodiesel Content on Performance and Regulated and Unregulated Emissions of a Diesel Engine Using Contour-Plot Map. *Science of the Total Environment*, **658**, 1117-1130.
https://www.sciencedirect.com/science/article/abs/pii/S0048969718351441
https://doi.org/10.1016/j.scitotenv.2018.12.270

[10] Qian, Y., Lili, L., Tiezhu, L. and Ran, T. (2022) Quantifying the Impact of Alternative Bus Stop Platforms on Vehicle Emissions and Individual Pollution Exposure at

Bus Stops. *International Journal of Environmental Research and Public Health*, **19**, Article 6552. https://www.mdpi.com/1660-4601/19/11/6552 https://doi.org/10.3390/ijerph19116552

[11] Lai, C.H., Hsiao, P.K., Yang, Y.T., Lin, S.M. and Lung, S.C. (2021) Effects of the Manual and Electronic Toll Collection Systems on the Particulate Pollutant Levels on Highways in Taiwan. *Atmospheric Pollution Research*, **12**, 25-32. https://www.sciencedirect.com/science/article/abs/pii/S1309104221000313 https://doi.org/10.1016/j.apr.2021.01.020

[12] Fontaras, G., Zacharof, N.G. and Ciuffo, B., (2017) Fuel Consumption and CO_2 Emissions from Passenger Cars in Europe Laboratory versus Real-World Emissions. *Progress in Energy and Combustion Science*, **60**, 97-131. https://www.sciencedirect.com/science/article/pii/S0360128516300442 https://doi.org/10.1016/j.pecs.2016.12.004

[13] DeFries, T.H., Sabisch, M., Kishan, S., Posada, F., German, J. and Bandivadekar, A.P. (2014) In-Use Fuel Economy and CO_2 Emissions Measurement Using OBD Data on US Light-Duty Vehicles. *SAE International Journal of Engines*, **7**, 1382-1396. https://www.sae.org/publications/technical-papers/content/2014-01-1623/ https://doi.org/10.4271/2014-01-1623

[14] Smit, R., Awadallah, M., Bagheri, S. and Surawski, N.C. (2022) Real-World Emission Factors for SUVs Using On-Board Emission Testing and Geo-Computation. *Transportation Research Part D: Transport and Environment*, **107**, Article ID: 103286. https://www.sciencedirect.com/science/article/abs/pii/S1361920922001146 https://doi.org/10.1016/j.trd.2022.103286

[15] SASO (2022) Executive Regulations for Organizing Periodic Technical Inspection of Vehicles, 1st Edition. https://www.saso.gov.sa/ar/Laws-And-Regulations/exeRules/Pages/the_Periodic_Technical_Inspection_of_Vehicles.aspx

[16] JCGM 200 (2012) International Vocabulary of Metrology-Basic and General Concepts and Associated Terms (VIM). 3rd Edition. https://www.bipm.org/documents/20126/2071204/JCGM_200_2012.pdf/f0e1ad45-d337-bbeb-53a6-15fe649d0ff1

[17] Magnusson, B. and Omemark, U. (2014) Eurachem Guide: The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics. https://www.eurachem.org/images/stories/Guides/pdf/MV_guide_2nd_ed_EN.pdf

[18] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP and OIML (1993) Guide to the Expression of Uncertainty in Measurement. 1st Edition. https://www.bipm.org/documents/20126/2071204/JCGM_100_2008_E.pdf/cb0ef43f-baa5-11cf-3f85-4dcd86f77bd6

[19] Shehata, A.B., Alyami, H.A., Alowaysi, A.S. and Alaskar, A.R. (2020) Preparation and Certification of Carbon Monoxide Gas Reference Material for the Quality of CO Emission Measurements. *Journal of Chemical Metrology Articles*, **1**, 11-24. https://www.acgpubs.org/doc/2021060321532358-JCM-2104-2055.pdf https://doi.org/10.25135/jcm.58.21.04.2055

[20] Shehata, A.B., Alyami, H.A., Alaskar, A.R. and Alowaysi, A.S. (2020) Development of CO_2 in N_2 Primary Gas Mixtures as Certified Reference Materials for Supporting the Climate. *Science Journal of Chemistry*, **10**, 133-143. https://www.sciencepublishinggroup.com/article/10.11648/j.sjc.20221005.11

[21] Shehata, A.B., Alyami, H.A., Alaskar, A.R. and Alowaysi, A.S. (2023) Certification

of a Multicomponent Reference Material from Natural Gas Mixture by Gravimetry and Dual GC-FID/TCD System. *Green and Sustainable Chemistry*, **13**, 269-290.
https://www.scirp.org/journal/paperinformation?paperid=129174
https://doi.org/10.4236/gsc.2023.134015

[22] International Council for Harmonization (2005) ICH Harmonized Tripartite Guideline, Validation of Analytical Procedures: Text and Methodology Q2 (R1).
https://www.fda.gov/media/152208/download

[23] Oman, Z. and Hary, B. (2015) Estimating Precision and Accuracy of GC-TCD Method for Carbon Dioxide, Propane and Carbon Monoxide Determination at Different Flow Rate of Carrier Gas. *Hemijska industrija*, **70**, 451-459.
https://doiserbia.nb.rs/img/doi/0367-598X/2016/0367-598X1500051Z.pdf
https://doi.org/10.2298/HEMIND150315051Z

[24] Shehata, A.B., AlAskar, A.R., AlRasheed, M.A., AlZahrany, A.M., AlKharraa, F.A. and Al Sowailem, S.A. (2023) Validation of a Method for the Measurement of Caffeine in Water by HPLC-UV. *Green and Sustainable Chemistry*, **13**, 291-302.
https://www.scirp.org/pdf/gsc_2023112911522943.pdf
https://doi.org/10.4236/gsc.2023.134016

[25] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP and OIML (1993) Guide to the Expression of Uncertainty in Measurement, 1st Ed.
https://www.bipm.org/documents/20126/2071204/JCGM_100_2008_E.pdf/cb0ef43f-baa5-11cf-3f85-4dcd86f77bd6

[26] Leito, I., Strauss, L., Koort, E. and Pihl, V. (2002) Estimation of Uncertainty in Routine pH Measurement. *Accreditation and Quality Assurance*, **7**, 242-249.
https://doi.org/10.1007/s00769-002-0470-2

[27] Eurachem/CITAC Guide (2013) Quantifying Uncertainty in Analytical Measurement. 3rd Edition.
https://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf