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Evaluation of EDXRF for the Determination of Elements in PM_{10} Filters

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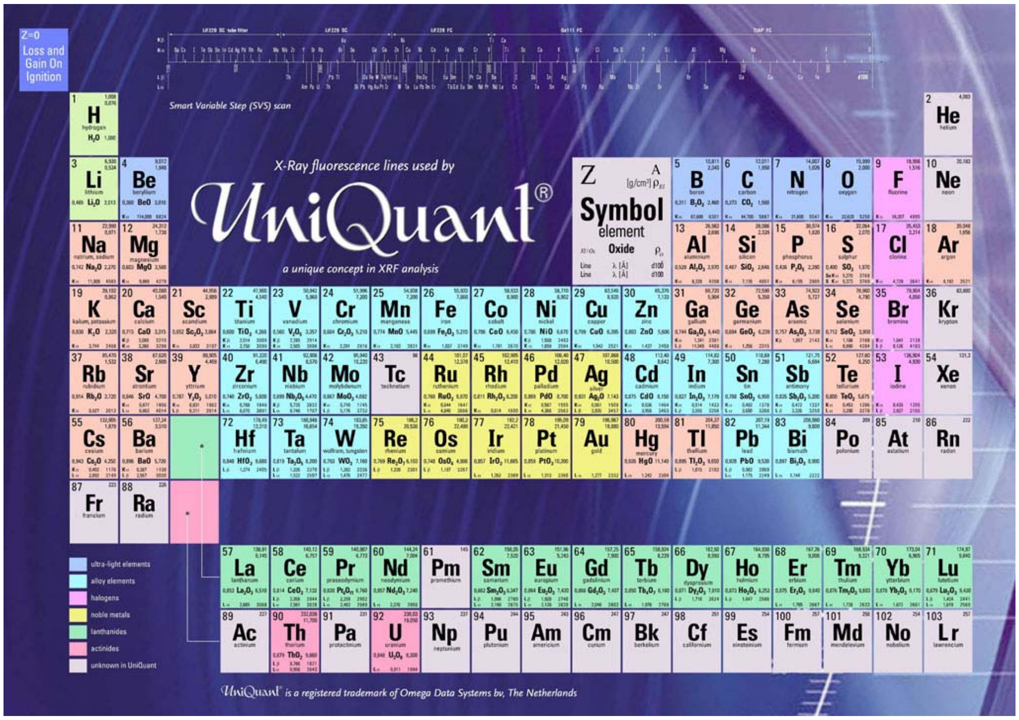

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Summary

The Joint Research Centre (JRC) has evaluated the potential of Energy Dispersive X-ray Fluorescence (EDXRF) to be equivalent to Graphite Furnace Atomic Absorption Spectrometers (GF-AAS) and Inductively Coupled Plasma Mass Spectrometer (ICP-MS) for the measurements of heavy metals in particulate matter (PM_{10}). The elements that are regulated in the European Directives for Air Quality (lead (Pb), arsenic (As), nickel (Ni) and cadmium (Cd)) and the ones included in the EMEP (Cooperative program for monitoring and evaluation of long-range transmission of air pollutants in Europe) programme, namely copper (Cu), chromium (Cr) and zinc (Zn) were tested. Other elements such as aluminium (Al), calcium (Ca), iron (Fe), magnesium (Mg), silicon (Si), chloride (Cl), potassium (K), sulphur (S), manganese (Mn), molybdenum (Mo), cobalt (Co), strontium (Sr), bromide (Br), titanium (Ti), tin (Sn) and antimony (Sb), which are essential for source apportionment studies were also tested. PM_{10} samples collected at different sites on Teflon (Pall Teflon) and 2 types of quartz filters (QMA and PallFlex) were analyzed both by EDXRF and ICP-MS.

The first objective of this study was to assess the suitability of the linear calibration of X-ray intensities versus PM-loaded standards for determining PM_{10}-bound elements on 3 types of filters loaded at several sampling sites. It was found that the linear calibration of EDXRF using loaded filters were found to be site and filter independent for Pb, Mn, Fe, Cu, Ti and Zn. Calcium was found to be site independent, but, filter type dependent. For Teflon filters, the linear calibration gave reasonably good results if calibration filters came from a similar site. The standardless EDXRF analysis was found to be more efficient than linear calibration for the quantification of most of the studied elements except As, V and Co. This calibration method is filter type and sampling site independent. Cd, Sn and Sb could not be analyzed, neither by the standardless EDXRF analysis nor the linear calibration in the studied samples.

The second objective was to check the ability of standardless EDXRF analysis to reach the Method Detection Limit (MDL) and Limit of Quantification (LOQ) requested in EN 14902 for monitoring As, Cd, Ni and Pb in PM_{10} loaded filters. It was found that MDLs of standardless EDXRF analysis were sufficiently low to measure Ni and Pb, but, not Cd and As, at the limit values of European Directives.

The third objective was to compare over a wide range of elemental masses and for several ambient air matrixes standardless EDXRF and ICP-MS analysis of PM_{10}-bound elements loaded on 3 types of filters (Teflon and 2 type quartz) in order to evaluate how well the two methods agree. It was found that the agreement between ICP-MS and standardless EDXRF results for Teflon filters were higher than quartz ones.

The forth objective was to estimate the measurement uncertainties of standardless EDXRF analysis and its major contributors according to the Guide to the Expression of Uncertainty in Measurement (GUM) used laboratory experiments. The uncertainties according to the GUM were found to be about 30% for most of the elements except for Ca, Fe, K, Zn, Mn, Ni, Ti (QMA), Cu and Ti (PallFlex) and Mo (Teflon), which their U_{GUM} at low concentrations sharply increased because of its poorer repeatability. The net intensities, initial calibration using thin film samples and sum of correlated variables, namely excited area, total deposition area and PM mass are the dominant contributors to measurement uncertainty. The uncertainties of Teflon filters were estimated lower than the others.

The fifth objective was to compare and confirm the GUM uncertainties with field measurements uncertainties estimated with the Guide to the Demonstration of Equivalence of Ambient Air Monitoring Method (Guide) using differences between co-located EDXRF and ICP-MS measurements. The field uncertainties decreased with elemental masses for almost all studied elements. The elemental mass threshold, which field uncertainty becomes equal to or less than GUM uncertainty, appeared for all elements except Cr, K, Mg and Ti for all types of filter. Hence, at higher

elemental masses than these thresholds, the proposed model equation for estimating the GUM uncertainty has demonstrated its validity and be used for whatever future filter analysis.

The last objective was to investigate the equivalence of standardless EDXRF analysis to ICP-MS for measuring As, Cd, Ni and Pb in PM_{10} according to the Guide and to demonstrate the ability of EDXRF to meet the Data Quality Objective (DQO) of the European Directives and EMEP manual (for As, Cd, Ni, Pb, Cr, Cu and Zn). It was found that The DQO of the EU Directive for Pb was met for all types of filter even at lower concentrations than the Limit Value. Only for Teflon, field uncertainty for Ni is likely to comply with the DQO. For As, the best results can be achieved by analyzing Teflon filter if using with linear calibration. It is likely that at the Limit Value the DQO can be met for As by linear calibration. Cd could not be quantified most probably due to low concentrations, and further tests at the Limit Value are required. The EMEP DQO was met for Cu (for Teflon) and Zn (for quartz filter), but, not for Cr.

As the overall result of this study, EDXRF can be considered as an alternative method to ICP-MS for measurements of PM-bound elements, particularly on Teflon filters. The European legislative requirements of Pb could be met for whatever filters type. The European legislative requirements of Ni and As are likely be met, but, it is unknown for Cd. The EMEP requirements can be met for Cu and Zn, but not for Cr. EDXRF can also be used to measure elements for source apportionment purposes. Calibrating the instrument by certified matrix matched standards on filter could produce better results, particularly for As, V and Co, even at low concentrations.

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Abbreviations

CRM: Certified Reference Material
DQO: Data Quality Objective
EDXRF: Energy Dispersive X-ray Fluorescence
GF-AAS: Graphite Furnace Atomic Absorption Spectrometry
ICP-MS: Inductively Coupled Plasma Mass Spectrometry
NIST: National Institute of Standards and Technology
PM: Particulate Matter
PM_{10}: PM with cut-off diameter equal to or less than 10 µm
$PM_{2.5}$: PM with cut-off diameter equal to or less than 2.5 µm
RD: Relative Deviation
RAD: Relative Absolute Deviation
RAD_m: Mean of Relative Absolute Deviation
RSD: Relative Standard Deviation
MDL: Method Detection Limit
LOQ: Limit of Quantification
QC: Quality Control Solution
S/B: Sample–to-blank Ratio
S&I: Shape and Impurity Factor
GUM: Guide to the Expression of Uncertainty in Measurement
U_{GUM}: Expanded Combined Uncertainty Estimated According to GUM
$U_{r,GUM}$: Relative Expanded Combined Uncertainty Estimated According to GUM
U_{DIR}: Expanded Combined Uncertainty Estimated According to Equivalence Method
$U_{r,DIR}$: Relative Expanded Combined Uncertainty Estimated According to Equivalence Method
EMEP: Cooperative Program for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe
QMA: Quartz filter, Whatman International Ltd (UK), model: 1851047
PallFlex: Quartz filter, Pall Corporation (USA), model: PallFlex 2500QAT-UP

1 Introduction and Objectives

Chemical content of particulate matter (PM) have been determined for a long time all around the world because of their toxicity (Schlesinger et al, 2006[1]; Kampa and Castanas, 2008[2]; Zhang et al, 2011[3]) and for source apportionment purposes (Hopke et al, 2003[4]; Liu et al, 2003[5]; Kim et al, 2003[6]; Viana et al, 2008[7]). They are analysed using sensitive wet chemistry based methods such as, Graphite Furnace Atomic Absorption Spectrometers (GF-AAS) and Inductively Coupled Plasma Mass Spectrometer (ICP-MS). However, these methods require labour intensive and expensive sample pre-treatment/analysis, and well qualified operators. Besides, sample pre-treatment may also cause contamination of samples even when the maximum attention is taken. As a result of the shortcoming of ICP-MS and GF-AAS, many researchers explore alternative analytical techniques.

The European air quality Directives (2004/107/EC[8] and 2008/50/EC[9], hereafter called EU Directives) state that GF-AAS or ICP-MS operated according to EN 14902[10] are the reference methods for the monitoring of As, Cd, Ni and Pb in PM_{10}, in order to detect exceedances of the limit values (LV) defined in the Directives. However, European legislation allows using an alternative method provided that its equivalence to the reference methods (GFAAS or ICP-MS) can be demonstrated following the Guide to the Demonstration of Equivalence of Ambient Air Monitoring Method[11] (hereafter called the Guide).

X-ray based analysis techniques have been intensively implemented for the determination of elements in several environmental matrixes such as air filters (Calzolai et al, 2008[12]; Canepari et al, 2009[13]; Niu et al, 2010[14]; Brown et al, 2010[15]; Ozturk et al, 2011[16]), stack gases (Haupt et al, 1997[17]) and soil

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(Chimidza et al, 2001[18]). X-ray analysis is faster and cheaper than ICP-MS and GF-AAS because it does not need any sample pre-treatment. Conversely to GF-AAS or ICP-MS, X-ray based techniques does not involve destruction of the samples being analyzed. This is a major advantage that makes further determinations of ions, organics and carbon still possible, which is essential for receptor models.

Typically, the determination of PM-bound elements using energy dispersive X-ray fluorescence (EDXRF) analysis includes establishing the relationship between X-Ray intensities and a set of calibration standards, in most cases, single element/compound thin films. However, these standards do not mimic the filter material and the PM matrix. Furthermore, the concentrations of single elements of those calibration standards are higher than their level in ambient air samples by orders of magnitude. The lack of commercially available matrix-matched standards for element in PM filters makes calibration the most challenging issue of EDXRF operation. Therefore, several researchers have been investigating an alternative calibration technique using the relationship between XRF intensities and elemental masses determined by a reliable analytical method such as ICP-MS. As demonstrated by several researchers[13,16], this technique gave satisfying results if the same PM sampling instruments and XRF is used at the same site of calibration. However, no study was found in the literature about the evaluation of the alternative calibration technique at a site different from the site of calibration. Apart from the typical calibration technique using single pure element/compound thin films, EDXRF can also be operated in standardless mode, which is expected to be sample matrix and concentration independent. The standardless EDXRF analysis is based on the only initial calibration with single pure element/compound thin films and further deconvolution of spectra that allows the determination of all elements in whatever sample matrix.

The objectives of this study were:

1) To assess the suitability of the linear calibration of X-ray intensities versus PM-loaded standards for determining PM_{10}-bound elements on 3 types of filters loaded at several sampling sites. The relationship between instrument responses and masses of elements determined by ICP-MS were used to establish the linear calibration;
2) To check the ability of standardless EDXRF analysis to reach the Method Detection Limit (MDL) and Limit of Quantification (LOQ) requested in EN 14902[10] for monitoring As, Cd, Ni and Pb in PM_{10} loaded filters;
3) To compare over a wide range of elemental masses and for several ambient air matrixes standardless EDXRF and ICP-MS analysis of PM_{10}-bound elements loaded on 3 types of filters (Teflon and 2 type quartz) in order to evaluate how well the two methods agree;
4) To estimate the measurement uncertainties of standardless EDXRF analysis and its major contributors according to the Guide to the Expression of Uncertainty in Measurement[19] (hereafter called GUM) used laboratory experiments;

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5) To compare and confirm the GUM uncertainties with field measurements uncertainties estimated with the Guide[11] using differences between co-located EDXRF and ICP-MS measurements;
6) To investigate the equivalence of standardless EDXRF to ICP-MS for measuring As, Cd, Ni and Pb in PM_{10} according to the Guide[11]. To demonstrate the ability of EDXRF to meet the Data Quality Objective (DQO) of the European Directives and EMEP manual (Cooperative program for monitoring and evaluation of long-range transmission of air pollutants in Europe, 2011[20]) for As, Cd, Ni, Pb, Cr, Cu and Zn.

This study is the first attempt to evaluate the quality of the standardless EDXRF analysis of PM_{10}-bound elements by comparison to ICP-MS including a wide variety of filter materials and different samples matrixes.

2 Experiments

2.1 Sampling of PM_{10}

PM_{10} loaded filters were sampled at several sites according to the requirements of EN12431 (1998)[21]. The sampling sites, filters, instruments and PM masses are summarized in Table 1. The flow rates of the PM_{10} samplers were adjusted using a certified gas counter at least twice a year. Prior to sampling, the sampler inlets were cleaned and greased. The flow rates, pressure and temperature sensors were checked at each site[22].

Loaded and blank filters were conditioned for at least 2 days at 50% relative humidity and 20 °C prior to weighing before and after sampling. The filters were weighted using a microbalance with 1-µg resolution (Mettler Toledo Switzerland, Model AX26) following the procedure of EN 14907[23].

Table 1. Field site of PM_{10} sampling, model of low volume samplers, filter type and range of PM_{10} mass

Location/Types of site/Number of filters	Date/Sampling Duration and Flow	PM_{10} Sampler	Filter	PM_{10} Range, mg
Bergamo (IT)/Urban (n=9)	19-27 Nov 2007 24 h, 2.3 $m^3 h^{-1}$	Leckel GmbH (D), SEQ47/50	PallFlex[a]	1.3-6.3
Milan (IT)/Urban (n=7)	07-21 Feb 2007 24 h, 1.11 $m^3 h^{-1}$	FAI s.r.l., HYDRA	Teflon[b]	1.4-3.6
Lodi (IT)/Urban (n=4)	27 Feb-13 Mar 2007 24 h, 1.15 $m^3 h^{-1}$	FAI s.r.l., HYDRA	Teflon[b]	0.3-1.7
Milan PO (IT)/Urban Background (n=8)	12-15 Jan 2008 4 h, 2.3 $m^3 h^{-1}$	FAI s.r.l., HYDRA	Teflon[b]	1.6-2.6
Port Tablot (UK)/Rural-Industrial (n=8)	24 Apr-7 May 2008 24 h, 2.3 $m^3 h^{-1}$	Leckel GmbH (D), SEQ47/50	QMA [c]	0.5-2.9

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[20] EMEP manual, 2011. Available at http://tarantula.nilu.no/projects/ccc/manual/index.html

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[23] European Standard, 2005. Ambient air quality - Standard gravimetric measurement method for the determination of the $PM_{2,5}$ mass fraction of suspended particulate matter. EN 14907. Brussels, Belgium. http://www.CEN.eu

Graz (AT)/Urban Background (n=5)	12-22 Oct 2006 24 h, 2.3 m^3 h^{-1}	Leckel GmbH (D), SEQ47/50	QMA [c]	1.8-4.1
Prague (CZ)/ Urban Background (n=5)	05-10 Nov 2006 24 h, 2.3 m^3 h^{-1}	Leckel GmbH (D), SEQ47/50	QMA [c]	0.5-3.0

IT: Italy; UK: United Kingdom; AT: Austria; CZ: Czech Republic, D: Germany
[a]: Pall Corporation (USA), model: PallFlex 2500QAT-UP, quartz
[b]: Pall Corporation (USA), model: Teflo R2PJ047
[c]: Whatman International Ltd (UK), model: 1851047, quartz

2.2 EDXRF Set up

All filters were analyzed using the ARL Quant'X (Thermo Scientific Inc, USA) EDXRF spectrometer according to the conditions given in Table 2. This spectrometer is equipped with an air cooled X-ray tube (Rh anode, 40 W maximum power, 4-50 kV voltage, 0.02-1.98 mA current), a peltier cooled Si(Li) drifted crystal detector (15 mm^2 crystal area, 3.5 mm crystal depth and 155 eV resolution), and a pulse processor (32 bit digital type, 20 eV channels, 1-40 ms adjustable shaping time, up to 100000 cps live count rate and 400-40960 eV energy range. Primary beam filters are placed in front of the X-ray beam in order to decrease the X-Ray energy to the correct excitation bandwidth of the elements to be analyzed.

The instrument was calibrated using pure thin film standards (Micromatter– XRF Calibration standards, 50 µg/cm², N - Nuclepore® polycarbonate aerosol membranes, USA). Since the levels of concentration of elements in PM_{10} sampled in ambient air are rather low, live times were increased in order to reach sufficient counts detected when analyzing a NIST CRM 2783 (see Table 2).

Before analysis, the filter holders and chamber of the EDXRF spectrometer were cleaned using dry filtered air. An energy adjustment and instrumental drift check were also performed prior to analysis using pure Cu and 10 pure thin film standards, respectively. The instrumental drift was evaluated taking as reference the counts registered at the initial calibration of the spectrometer. In case of drift higher than 10%, the instrument was subjected to proper maintenance in order to diminish these deviations. The samples were analyzed under vacuum with 3 replicates.

Table 2. Operational parameters of EDXRF. Primary beam filters are used to adjust X-Ray energy for the elements of interest. Voltage is the potential difference applied. Live time is the excitation/analyzing duration

Beam Filter	Voltage (kV)	Live Time, sec	Element
Cu Thick	50	240	Sn, Sb
Cu Thin	50	800	Mo, Cd
Pd Thick	30	1600	As, Br, Sr, Pb
Pd Medium	20	960	Cu, Zn
Pd Thin	16	600	Fe, Co, Ni, Mn
Aluminum	12	1000	Ti, V, Cr
Cellulose	8	200	S, Cl, K, Ca
No Filter	4	100	Mg, Al, Si

The quantifications of elements in PM_{10} were carried out using UniQuant, a special software based on the solution of Sherman equation (Sherman, 1955[24]) by the fundamental parameters method. The correctness of the solution was previously presented by Rousseau (2006[25]). With the UniQuant's

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[24] Sherman, J., 1955. The theoretical derivation of fluorescent X-ray intensities from mixtures. Spectrochimica Acta 7, 283–306

[25] Rousseau, R.M., 2006. Corrections for matrix effects in X-ray fluorescence analysis-A tutorial. Spectrochimica Acta - Part B Atomic Spectroscopy 61, 759-777

concept, instead of instrumental calibration relying on calibration of XRF intensities according to the mass of standards, instrumental sensitivity is determined as the function of net intensity and mass (Intensity/mass) which is constant and sample independent leading to standardless operation. The details of the software can be found elsewhere (www.uniquant.com). Deconvolution is applied to calculate spectra, which is unknown to the authors, since UniQuant is a commercial product. The software enables calculation of elemental concentrations using insensitivities, matrix type, instrumental drifts, matrix chemistry and measuring atmosphere. In this study, UniQuant (version 6.09, 2008[26]) was modified to measure elements in PM_{10} collected on filters. Will De Jongh slightly modified the Sherman equation giving the mass of element. In fact, elemental mass, c_i (ng), is calculated using Equation 1 where I_i is the drift corrected fluorescence intensities (counts/sec, cps), I_0 is the interference and drift corrected background modeled by UniQuant using filter type (cps). μ_i is the mass absorption coefficient of element i (cm^2/g). W_i is the weight factor of oxides assuming that all elements exist at the highest oxidation states (calculated from stoichiometry) for element i. K_i is the ratio of counts to mass of element i (cps/g) determined using thin film standards samples of pure elements (Initial calibration). A is the excited area (cm^2) of the filter to which the X-ray excitation is applied (No collimator used) whereas A_d is PM deposition area on filter (cm^2). m_{PM} is the excited PM mass in ng. The software calculates the interference for each measured elements, using a secret algorithm. The interfering elements and their masses are given by the software. The sum of interferences is subtracted to compute the concentrations of elements.

$$c_i = \left[\frac{(I_i - I_{i0})\mu_i}{W_i A K_i} - \sum Interference \right] \frac{A_d}{A} m_{PM} \qquad \textbf{Equation 1}$$

Actually, the first part in square brackets is the standard equation of the software to calculate the elemental mass ratio (mass of element/total mass). Subsequently, they are multiplied by A_d/A and m_{PM} to be converted to the total mass of element loaded on each filter, assuming evenly distribution of the particulate matter on filters and the absence of PM evaporation in the measuring chamber. The filter-specific parameter obtained by blank filter measurement, the so-called Shape and Impurity factor (S&I), is used to construct the background during the analysis with employed excitation energy and efficiency of measurement channel. The software needs information about the constituents of PM which cannot be excited by X-ray, for instance, C, H and N contents (Hereafter called Rest). Hence, approximate knowledge of PM in samples is required in order to select most appropriate Rest option. Several measurements cases according to the physical/geometrical data of sample (i.e., known Rest, unknown excitation area, being mono/multilayer etc.) were introduced in the software, and one was developed for air filters analysis. Chemistry of sample (i.e., element, oxides, etc.) has to be introduced to the software.

The repeatability of the standardless EDXRF determinations was assessed analyzing at least 6 times one loaded filter of each type (high PM loaded Pall (PallFlex) and Whatman quartz (QMA) and low loaded Teflon) and a NIST CRM 2783 within the same run. The relative standard deviations (RSD) were less than 10% for all elements and filter types, except Co (57%), Cd (151%), Sn (34%) and Sb (48%) for QMA (V and As below detection limit), Cr (22%), Sn (14%) and Sb (78%) for Pall quartz, V (111%) and Sn (26%) for Teflon and Co (70%), Sr (23%) and Sn (54%) for CRM 2783, which can be attributed to the low concentration. The reproducibility of standardless EDXRF results was determined by analysis of variance using the analytical results obtained for the same filters on 2 different days. No significant differences were found (for all elements and filters types).

Blank filters, drawn from the box of filters used for sampling, were analyzed concurrently in order to establish S&I factors of each filter types. These S&I factors were then optimized for all elements of the 8 Primary beam filters (see Table 2). The background is modeled by the software based on S&I and instrumental conditions. The field blanks and other blank filters from the same boxes were measured

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[26] Software UniQuant, Version 6.09, 2008. Thermo Fisher Scientific, The Netherlands

as samples to check how well the background and blanks fit. Very low (close to 0) net intensities were found, meaning that the modeled backgrounds based on only one S&I correspond to the blanks of the filter used for sampling. The estimation of elements by standardless EDXRF analysis is based on the mass closure of PM sample, denoting that the non-excited elements lighter than Na have to be accounted for in the mass estimation. Hence, assumptions of the extent of the unaccounted constituent of PM have to be introduced into the software. It was also assumed that all elements in PM_{10} existed in oxide form and that the majority of PM_{10} was made of elemental and organic carbon. Oxides and C, H, N mixtures were selected for Teflon filters, as Chemistry and Rest, respectively. Given that, quartz filters contained a huge amount of Si, a new Rest material, mixture of C, H, N and Si was established to analyze these samples.

The minimum X-ray penetration depth for 4 kV was estimated to be 0.77 µm. This figure exceeds the maximum PM thickness on filter of 0.22 µm calculated assuming 2 g cm^{-3} of density (Pitz et al[27] found 1.05 to 2.36 g cm^{-3} for $PM_{2.5}$ in Germany). Thus, the X-rays could reach and excite all particles deposited on the filters.

2.3 ICP-MS

The digestion of Teflon and PallFlex samples was carried out with 4 ml HNO_3, 2 ml H_2O_2, 1 ml HCl and 1 ml HF (Ultra pure, Romil Ltd., UK) using Milestone Microwave Labstation Ethos 900 (Italy). Field blanks and certified urban dust (NIST 1648) were digested and analyzed along the samples. The ICP-MS (Agilent Technologies Inc, Japan, 7500c) was used to quantify Mg, Al, K, Ca, Ti, V, Cr, Fe, Co, Ni, Mn, Cu, Zn, As, Sr, Pb, Mo, Cd, Sn and Sb. ICP-MS was calibrated using certified multi-element standards (BDH, USA) and analyses were started only when its correlation coefficient, r, were higher than 0.999. Sc, In and Tl were added as internal standards to all calibration standards, quality control (QC) solutions and samples in order to evidence any drifts of the mass spectrometer. The instrumental drift was checked by analyzing a QC sample every 5 samples and the drifts were corrected linearly between 2 QCs. The average sample to blank ratios (S/B) varied between 1.4 (Zn) and 66 (Fe) for Teflon, and between 1.8(Al) and 45 (V) for PallFlex. The absolute average ICPMS biases of the NIST 1648 remained lower than 10%, except for Zn (19%), Fe (14%) and K (17%).

The QMA filters were digested using Milestone Microwave Labstation Ethos 900 (Italy) following the procedure given in EN 14902. Briefly, 8 ml ultrapure HNO_3, 2 ml ultrapure H_2O_2 and 0.1 ml HF (Ultrex, JTBeaker) were added into Teflon vessels and then, they were placed in Milestone Microwave Labstation Ethos 900 (Italy). By addition of HF, it was aimed to enhance the recovery efficiencies.

The Teflon vessels were pre-cleaned using the same digestion program followed by 3 times rinsing with de-ionized water and dry in an oven at 150 ºC, prior to usage. The sample containers (PTFE flasks) were soaked at least over night with 10% HNO_3, followed by3 times rinsing with the same acid, 3 times with de-ionized water and dry in an oven at 50 ^oC. The sample tubes of autosampler were cleaned with the same procedure, but, dried with filtered dry air jet.

The ICP-MS was calibrated using certified mono-element standard solutions (Romil Ltd, UK, PriAg-xtra Series). Calibration curves were established analyzing freshly prepared calibration solutions, and they were accepted only if correlation coefficients (r) were >0.999. The QC solution, prepared independently from calibration solutions, was analyzed just after the establishment of calibration curves, every 10 samples and at the end of sequence. The instrument was re-calibrated, if the drift exceeded 10%. The deviation during the analysis was corrected assuming the instrumental drift was linear. Sc, Y, In and Tl were added as internal standards.

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[27] Pitz, M., Schmid, O., Heinrich, J., Birmili, W., Maguhn, J., Zimmermann, R. et al., 2008. Seasonal and diurnal variation of $PM_{2.5}$ apparent particle density in urban air in Augsburg, Germany. Environmental Science and Technology 42, 5087-5093

NIST 1648 samples were digested and analyzed following the same procedures of QMA. Adding HF improved the recoveries of Cr from 50% to 86%, of Al from 60% to 103%, of K from 55% to 99%, and of Ti from 51% to 93%, as average. All the other recoveries remained between 90-110 %.

Owing to high content in the filter materials, the S/B of terrestrial elements such as Al, K, Mg, Ca, Ti and Cr (not terrestrial) were found between 1-2 whereas those of the trace elements and Fe were generally >5 except As for Graz and Prague (1.5).

2.4 Data Evaluation

Four types of data treatment were carried out:

- First, as an alternative to the calibration using certified thin film samples, the linear calibration with standards consisting of loaded filters analyzed by ICP-MS versus XRF intensities were plotted. The evaluation was carried out using the analytical results of a set of loaded filters that was also analyzed by ICP-MS and CRM 2783. For QMA filters, the possible influence of the choice of sampling site on the EDXRF calibration functions was assessed by comparing the agreement between 2 functions of calibrations using filters of at one urban and one industrial sites.
- Second, it was checked if standardless EDXRF analysis could reach the limits of detection and quantification that are requested in EN 14902.
- Third, the agreement between ICP-MS and standardless EDXRF analysis was evaluated.
- Finally, the standardless EDXRF measurement uncertainties and its main contributors were estimated using the GUM method. The GUM uncertainty (hereafter called U_{GUM}) can be estimated for any sample. However, the reliability of this estimation strongly depends on the ability of Equation 1 to accurately describe the EDXRF measurement principle and on the accuracy of the estimation of each contributing parameter given in Equation 1. In order to demonstrate the U_{GUM} validity, the measurements uncertainties were also estimated using based on the Guide for the Demonstration of Equivalence of Measuring Methods, actually the differences between ICP-MS and EDXRF analysis of filters loaded at co-located field sites. Differences between the two methods of uncertainty estimations were evidenced and the likely causes were discussed.

2.4.1 Linear Calibration Using Standards Analyzed by ICP-MS

EDXRF was calibrated by establishing a linear regression between elemental masses of loaded filters obtained by ICP-MS analysis (m, in ng) and XRF intensities (in counts per second divided to tube current, cps/mA of the X-ray tube) given in Equation 2. The expanded uncertainty of the EDXRF values, U (m_{EDXRF}), is estimated using Equation 3 (Miller and Miller, 1986[28]) at the central point of each mass ranges.

$$I_{EDXRF} = b_0 + b_1 m_{ICP-MS}$$

Equation 2

$$U\left(m_{EDXRF}\right) = k\left[\frac{\sum\left(I_i - \left(b_0 + b_1 m_{i,ICP-MS}\right)\right)^2}{n-2}\right]^{½} / b_1 \left[1 + 1/n + \frac{\left(I - \bar{I}\right)^2}{b_1^2 \sum\left(m_{i,ICP-MS} - \bar{m}_{ICP-MS}\right)^2}\right]^{½}$$

Equation 3

where I is the XRF intensities (cps/mA) of the measured sample (middle point of the range), I_i is the intensities of standard i, $\bar{I}$ is the average intensities of all standards. m is the elemental masses determined by ICP-MS or EDXRF, $\bar{m}_{ICP-MS}$ is the average elemental masses of all standards, n is the number of standards used for calibration. The coverage factor, k, was set to 2. The relative expanded

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[28] Miller, J.C., Miller, J.N., 1986. Statistics for Analytical Chemistry, John Wiley and Sons, New York

uncertainty of EDXRF measurements, U_r. (m_{EDXRF}), corresponds to the ratio of U(m_{EDXRF}) out of m_{EDXRF} of the measured sample.

Linear calibration lines were established using Teflon filters loaded in two urban sites (Milan and Lodi, n=11, hereafter called Teflon-Urban). Other filters loaded at an urban background site (Milan PO) were analyzed by ICP-MS and EDXRF both by linear calibration and standardless analysis. The differences between linear calibration and ICP-MS from one side and standardless EDXRF analysis and ICP-MS from another side were calculated. A CRM 2783 was also analyzed by linear calibration and standardless analysis. The differences between the analyses and certified values of CRM 2783 were computed.

Two linear calibrations were carried out for QMA filters, one using the filters of a rural-industrial site (Port Talbot-UK, n=8, hereafter called QMA-Industrial) and one with the filters of 2 urban sites (Graz, n=5 plus Prague, n=5, hereafter called QMA-Urban). One QMA filter loaded at an urban site, whose analysis by several laboratories (Gerboles et al, 2011[29]) could be used as reference values, was analyzed using these two linear calibrations and standardless analysis. The differences between EDXRF determinations and reference values were calculated and compared. The linear calibration curves of PallFlex were established, however, due to lack of sample from another site or reference, the comparison with the standardless EDXRF analysis was not performed

2.4.2 Method Detection Limits (MDLs) and Limits of Quantification (LOQs)

The theoretical method detection limits (MDLs) and limits of quantification (LOQs) of EDXRF were calculated as 3 and 10 times of standard deviation of the underlying background (SD), respectively (Johansson et al, 1995). The masses equivalent to 3 and 10 times SD of each background were calculated using Equation 1 for MDLs and LOQs, respectively.

2.4.3 Comparison of ICP-MS and Standardless EDXRF Analysis

The results of ICP-MS and standardless EDXRF analysis were evaluated by relative deviation (RD) and relative absolute deviation (RAD) calculated by Equation 4 and Equation 5, respectively.

$$RD(\%) = \left(\frac{m_{EDXRF} - m_{ICP-MS}}{m_{ICP-MS}} \right) 100 \qquad \textbf{Equation 4}$$

$$RAD(\%) = \left(\frac{\left| m_{EDXRF} - m_{ICP-MS} \right|}{m_{ICP-MS}} \right) 100 \qquad \textbf{Equation 5}$$

where, m refers to the mass of elements (ng) determined by standardless EDXRF analysis or ICP-MS. The RD values were plotted against masses of ICP-MS in order to see the agreement between the two methods, and also to assess the relationship between elemental masses and deviations. All filters of the measuring campaigns (see Table 1) were divided in three groups according to their filter type. The RADs of each filter were calculated. Finally, the means of RAD (RAD_m) for each group and standard deviations s(RAD) of all RADs were computed to evaluate the extent of deviations between two methods over the whole range of elemental masses.

2.4.4 Measurement Uncertainty

Equation 1 contains variables whose estimation is unknown to the authors, e. g. μ_i and interference correction. The interferences are predefined by the software for each element and lines, and the list of

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[29] Gerboles, M., Buzica, D., Brown, R.J.C. , Yardley, R.E., Hanus-Illnar, A., Salfinger, M. et al., 2011. Interlaboratory comparison exercise for the determination of As, Cd, Ni and Pb in PM_{10} in Europe, Atmospheric Environment 45, 3488-3499

interfering elements with their concentrations (mass/mass) is given as output. The relative expanded uncertainties ($U_{r,GUM}$) for elements analyzed by EDXRF were estimated using Equation 6, obtained by the application of the GUM method. Equation 6 was set up assuming that the only significant correlations appear between A_d and m_{PM} (r=-1) and A and m_{PM} (r=1). In Equation 6, the nomenclature is the same as in Equation 1 whilst ∑int and I_{net} denote the sum of interfering elements and net intensity (I_i–I_{i0}), respectively. It is possible that other parameters of Equation 1 are correlated. However, these correlations cannot be quantified, due to unknown equations for calculations by the authors (for example between A, K and μ).

$$U_{r,GUM} = k\frac{u\ (c_i)}{c_i} = k\sqrt{\begin{gathered}\left[\frac{\mu_i I_{net}}{c_{i\%}AK_i}\right]^2\left(\frac{u(I_{net})}{I_{net}}\right)^2+\left[\frac{\mu_i I_{net}}{c_{i\%}AK_i}\right]^2\left(\frac{u(\mu_i)}{\mu_i}\right)^2+\left[\frac{\mu_i I_{net}}{c_{i\%}AK_i}\right]^2\left(\frac{u(K_i)}{K_i}\right)^2+\left[\frac{\mu_i I_{net}}{c_{i\%}AK_i}+1\right]^2\left(\frac{u(A)}{A}\right)^2 \\ +\left[\frac{\sum \mathrm{int}}{c_{i\%}}\right]^2\left(\frac{u(\sum \mathrm{int})}{\sum \mathrm{int}}\right)^2+\left(\frac{u(A_d)}{A_d}\right)^2+\left(\frac{u(m_{PM})}{m_{PM}}\right)^2+ \\ 2\left[-2\frac{u(A)}{A}\frac{u(m_{PM})}{m_{PM}}r(A,m_{PM})+\frac{u(A_d)}{A_d}\frac{u(m_{PM})}{m_{PM}}r(A_d,m_{PM})\right]\end{gathered}} \qquad \textbf{Equation 6}$$

The repeatability of I_i, I_{i0} and instrumental drift were only taken into account, due to lack of the equation used to estimate I_{i0}. I_{i0} is computed by the software on the basis of filter surface (S&I) and excitation energy and efficiency of measurement channel. Furthermore, Rest was thought to be able to affect the continuum of background spectra. Thus, apart from drift and repeatability, the manual optimization of S&I and selection Rest type were counted as uncertainty sources of I_{i0}. The standard uncertainty of I_{i0} was evaluated by using different types of Rest (n=3), PM chemistry (Oxides and elemental state) and differently optimized S&I (n=3). S&I is a continuum where the cps/mass (and florescence energy are inversely proportional. The S&I is constructed using the measuring intensities in element specific channels. Manual optimization of S&I denotes making the continuum consistent with the neighboring channels, by removing spikes. The equation of μ_i is also unknown to the authors. Thus, the standard uncertainty of μ_i was evaluated as the quadratic sum of contributions from repeatability, different S&I, matrix chemistry and Rest. The effect of different S&I on μ_i was very limited, and only compatible Rest and Chemistry with PM constituents were selected. K_i was determined analyzing of thin film standards, and optimized manually. K_i is also a continuum as a function of cps/mass and florescence energy. Thus, the standard uncertainty of K_i was computed by quadratic summation of standard uncertainties of elemental density of thin film samples, manual optimization of continuum and excited area. The uncertainty of W_i was not considered, since this parameter was assumed to be a known and constant. The uncertainties of excited and deposited areas, A and A_d, were calculated assuming 1 mm of standard uncertainty on the diameter. The diameter of the X-ray excitation beam was found to be 16 mm on an X-ray excited plate of barium sulfate. The deposition areas of each filter type were measured using a caliper. The uncertainty of m_{PM} was estimated as the quadratic summation of the balance's standard uncertainty and repeatability. The repeatability of the sum of interferences in 3 replicates of measurements was used to estimate the standard uncertainty of this interference correction. The coverage factors, k, were estimated using the effective degree of freedom calculated by Welch-Starrethwaite formula presented in Annex G of the GUM, at the 95% confidence level.

The relative expanded uncertainty can also be estimated using the method described in the Guide that depends on the differences between co-located pairs of loaded filters analyzed by EDXRF and ICP-MS ($U_{r,DIR}$). This method assumes a linear relationship between the measurement results of candidate (m_{EDXRF}) and reference ($m_{ICP\text{-}MS}$) methods as shown in Equation 7. The relative expanded uncertainty of EDXRF measurements U_{DIR} (m_{EDXRF}) is calculated using Equation 8, where RSS is the square sum of residuals resulting from the orthogonal regression, $u(m_{ICP\text{-}MS})$ is the random uncertainty of the ICP-MS method calculated using standard deviations of 10 repeated measurements. The last term gives the bias of the candidate method for the elemental mass determined by ICP-MS. Division by m_{EDXRF} was preferred; because, when a sample will be analyzed using EDXRF, the reference/true value measured by ICP-MS will be unknown. The algorithm to estimate the values for b_0 and b_1 together with their uncertainty is given in the Guide. It aimed at minimizing of the error function consisting of the sum of residuals between the linear line and the EDXRF masses plus the residuals between the linear line and the ICP-MS masses. In this study, since all the residuals were constant, the RSS could be calculated using the simple Equation 9. EDXRF and ICP-MS masses lower than MDLs were discarded from calculations.

Equation 7

$$m_{EDXRF} = b_0 + b_1 m_{ICP-MS}$$

Equation 8

$$U_{r,DIR}(m_{EDXRF}) = k\frac{u_{DIR}}{m_{EDXRF}}(m_{EDXRF}) = k\sqrt{\frac{(RSS/n-2) - u(m_{ICP-MS})^{\;2} + [b_0 + (b_1 - 1)m_{ICP-MS}]^2}{m_{EDXRF}^2}}$$

Equation 9

$$RSS = \sum_{i}^{n}(m_{EDXRF\,i} - b_0 - b_1 m_{ICP-MS})^2$$

The relative contributions of RSS (r-RSS) and bias(r-Bias) defined in Equation 8 were computed to evaluate their contributions to $U_{r,DIR.}$ To do that, the contribution from u (m_{ICP-MS}) was ignored and the r-RSS was calculated as the division of first term of Equation 8, namely (RSS/n-2)/(m_{EDXRF})^2, to the square of $U_{r,DIR}$. Similarly, r-Bias was calculated using the last term of Equation 8 and the square of $U_{r,DIR}$.

Finally, $U_{r,DIR}$ and $U_{r,GUM}$ were compared. In fact, $U_{r,DIR}$ lower or similar than $U_{r,GUM}$ would indicate that Equation 6 can be applied to any standardless EDXRF measurement to correctly estimate $U_{r},_{GUM}$ without the need for further field experiments. Conversely, if $U_{r,DIR}$ would be higher than $U_{r,GUM}$, one would assume that Equation 6 does not cover all the sources of uncertainties, e. g. the interference correction through the Sherman equation. More field comparisons of ICP-MS and EDXRF analysis would be needed to estimate $U_{r,DIR}$ at any type of sampling site that is not investigated in this study.

It was also checked if the measurement uncertainties of EDXRF, $U_{r,GUM}$ and $U_{r,DIR}$, could reach the data quality objectives (DQO) at the limit values of Cd (40% at 5 ng m^{-3}), As (40% at 6 ng m^{-3}), Ni (40% at 20 ng m^{-3}) and Pb (25% at 500 ng m^{-3}) of the European Directives. However, no concentrations of this study were close enough to the limit values. Therefore, we decided to estimate $U_{r,DIR}$ at limit values by extrapolation. Unfortunately, Cd and As could not be measured by standardless EDXRF analysis in this study, probably due to low concentrations found of our samples. The measurement uncertainties of Zn, Cu and Cr were also checked with respect to the EMEP DQO (25%).

3 Results and Discussion

3.1 Evaluation of Linear Calibration and Standardless EDXRF Analysis

The calibration lines established using the net XRF intensities and elemental masses determined by ICP-MS are plotted in Figure 1 for Teflon filters at urban site and for QMA filters at urban and industrial sites. No ICP-MS results of Si, Cl, S, Br (for all the filters), Mo and Sr (only for QMA) were available, and therefore, these elements could not be evaluated. Cd, Sn and Sb could not be analyzed, neither by the standardless EDXRF analysis nor the linear calibration in the studied samples. The coefficients of determination, R^2, are also given in the figure. In most of the case, R^2 values were higher for Teflon filters than for quartz filters.

Four patterns were observed for the calibration lines of Teflon and QMA filters. First, for Fe, Pb, Cu, Mn and Ti, the slopes were similar (the differences between slopes are less than 40%) for whatever type of filter or sampling site. Second, for Ca, the slopes of QMA filters at the urban and industrial sites were similar, but, they were different than the ones of the Teflon filters (filter effect). Third, for Zn, the slopes of QMA filters and Teflon filters at urban sites were similar, but, they were different from the ones at the Industrial site (QMA). This could be attributed to the lower concentration at the industrial site for Zn. Fourth, the slopes and intercepts of QMA at the urban and Industrial sites were different for K, As, V and Zn (site effect). Furthermore, no significant correlation could be evidenced between EDXRF and ICP-MS results for Mg and Ni at the urban sites and for Al and Cr at the industrial site. These constitute a clear sign for the dependence of the calibration on the sampling site likely caused by matrix effect that may prevent the linear calibration approach if samples of different origins have to be analyzed by EDXRF.

The relative expanded uncertainty, U_r (m_{EDXRF}), estimated in the middle of the mass ranges are plotted against R^2 in Figure 2 for QMA filters (loaded at 2 urban sites and at an industrial site) and in Figure 3 for Teflon filters. High R^2 and low U_r (m_{EDXRF}) were found for each type of filters for Pb, Fe, Mn and Cu (except for QMA at the industrial site). The Teflon filters results showed higher R^2 and lower U_r values than the QMA ones for all elements except Ni-Industrial and Ti at the urban and industrial sites. These might be attributed the lower concentration levels on Teflon filters than on QMA ones. The mass of Ni on the Teflon filters ranged between 150-550 ng, whilst the Ni-masses on QMA at the industrial site were between 400 and 3300 ng. Ti-masses on the Teflon filters were 150-1400 ng, whilst Ti-masses on QMA at the urban and industrial sites were 600-2400 and 570-1820 ng, respectively.

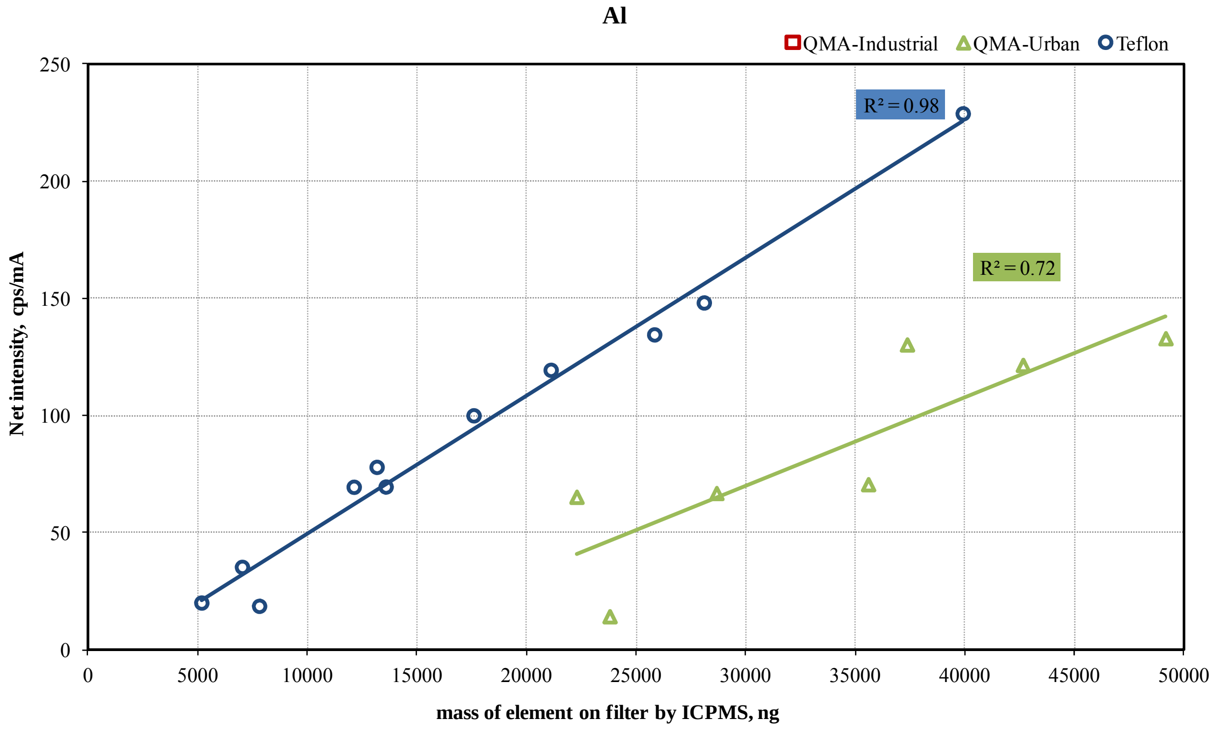
Differences between ICP-MS or reference values and EDXRF (quantified both by linear calibration and standardless EDXRF) were evaluated on the Teflon filters loaded at the Milan PO sampling site and on the NIST CRM 2783. The differences are plotted in Figure 4. The analysis of Milan PO Teflon filters by linear calibration resulted in mean absolute deviations lower than 30% for all elements except As (33±21%, mean±SD), Ca (38±25%), Co (34±18%), K (33±9%), Ni (43±17%) and Zn (37±8%). The mean absolute deviations of standardless EDXRF analysis on the same Milan PO filters were lower than 15% for Cr, Cu, Fe, K, Mg, Mn, Mo and Ti whereas they remained between 15-25% for the other elements except Ni (38%) (As, Co and V could not be quantified by the standardless EDXRF analysis). The mean absolute deviations of standardless EDXRF analysis for the Milan PO filters were lower than the ones using linear calibration except for Al, Pb and Sr. For the NIST CRM 2783, the deviations to certified values of standardless EDXRF analysis remained much lower than the ones the linear calibration of Teflon filters.

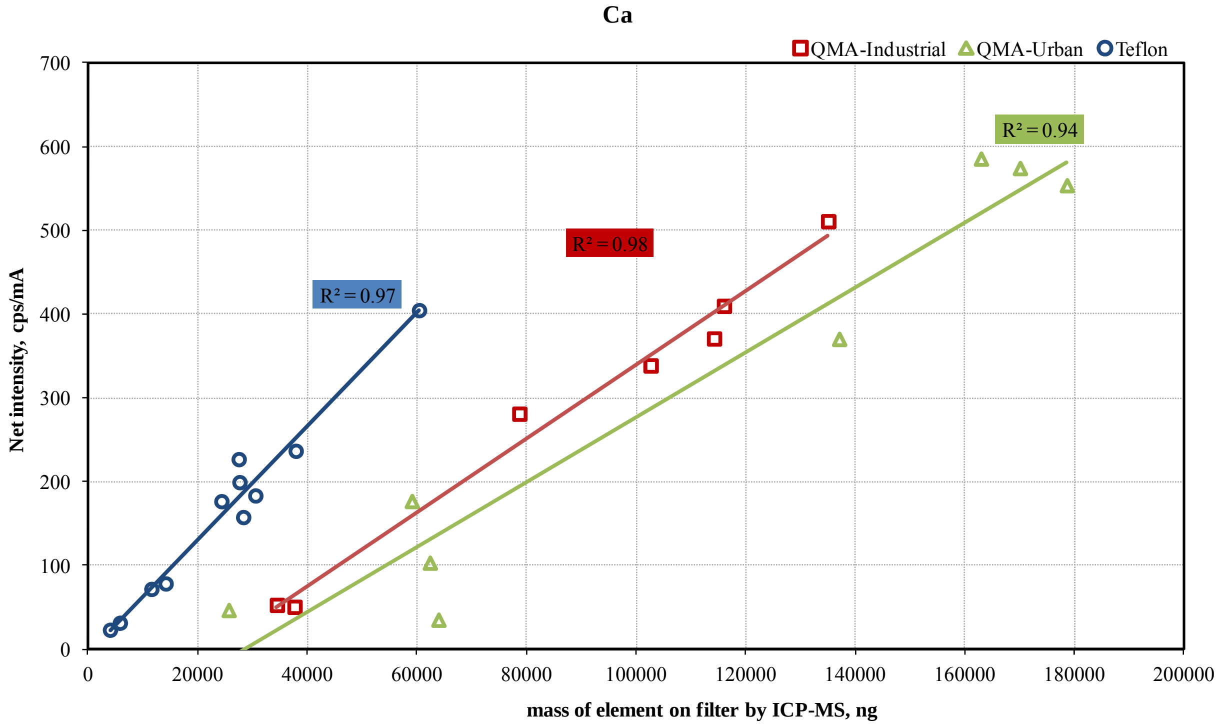
On Teflon filters, the R^2 and U_r (m_{EDXRF}) for As (see Figure 3) were found to be 0.91 and 49%, respectively, at the middle point of mass range (8-100 ng). The mean deviation of linear calibration of Milan PO was -33±21% (mass range: 40-75 ng), a reasonable result for As. However, the deviation of NIST CRM 2783 was found to be -175%, which might be attributed to low As-mass (11 ng) or to a matrix effects between the Teflon loaded filters used for calibration and the polycarbonate filter of NIST CRM 2783.

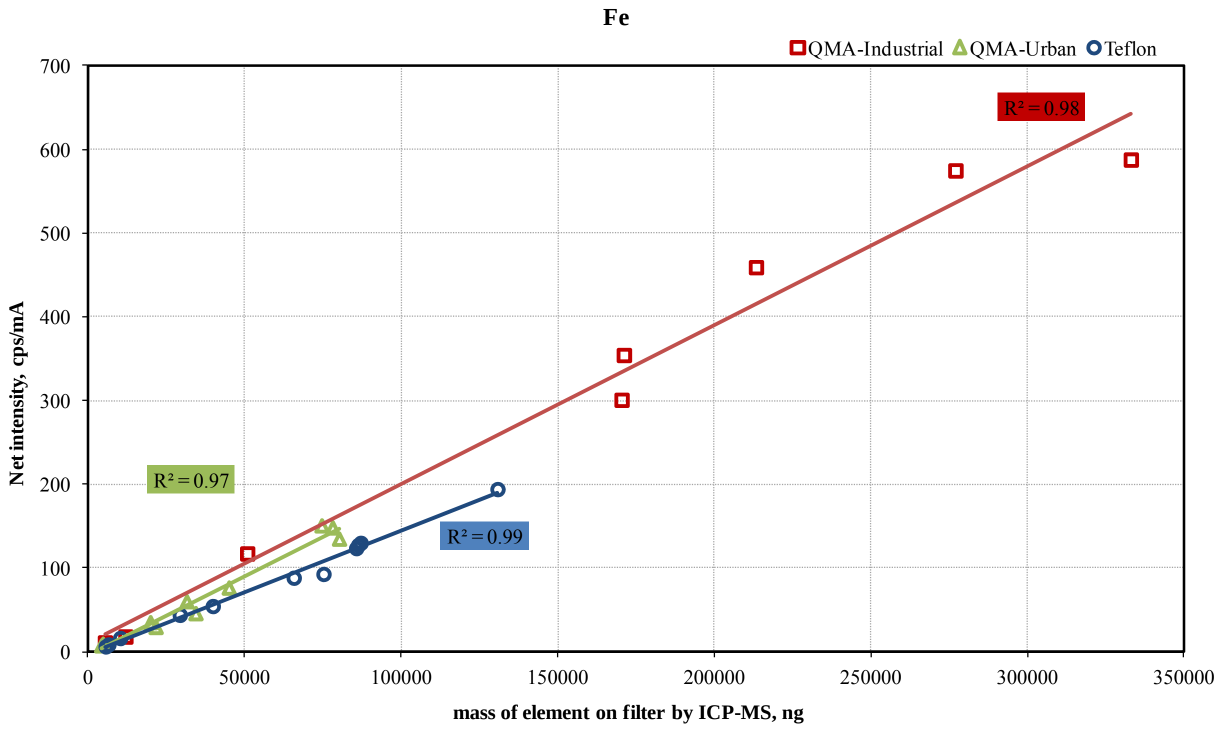
R^2 and U_r (m_{EDXRF}) for V on Teflon filters (see Figure 3) were found to be 0.88 and 43%, respectively, at the middle point of the mass range (20-224 ng). The mean deviation of linear calibration of Milan PO (mass range 40-110 ng) was 17±12% (see Figure 4). However, for the NIST CRM 2783, the deviation was up to 57%, even though the V mass (48 ng) was in the range of calibration.

For the reference QMA urban filter (QMA-Ref) tested in an intercomparison exercise (Gerboles et al., 2011)[29], the deviations between standardless EDXRF analysis and the reference values for Fe, Mn, Ni and Pb were lower than the ones between QMA-Ref and EDXRF analysis with linear calibration. Standardless EDXRF analysis showed higher deviation than linear calibrations for Cr and Zn when standard filters were loaded at QMA-Urban and at QMA-Industrial, respectively. Using linear calibration with the QMA-Industrial filters, the absolute deviations for Mn, V, Pb, Zn and Cu on QMA-Ref were equal to or lower than 20%, while using linear calibration with the QMA-Urban filters, the absolute deviations for Mn, Fe, Pb, Cu, Zn, V and As were found to be equal to or lower than 20%. For Ni determination on QMA-Ref using linear calibration with the filters of QMA-Industrial, the deviation from reference value was found to be high (516%) (see Figure 4), showing the dependence of the calibration line on the type of sampling site (industrial vs urban) .

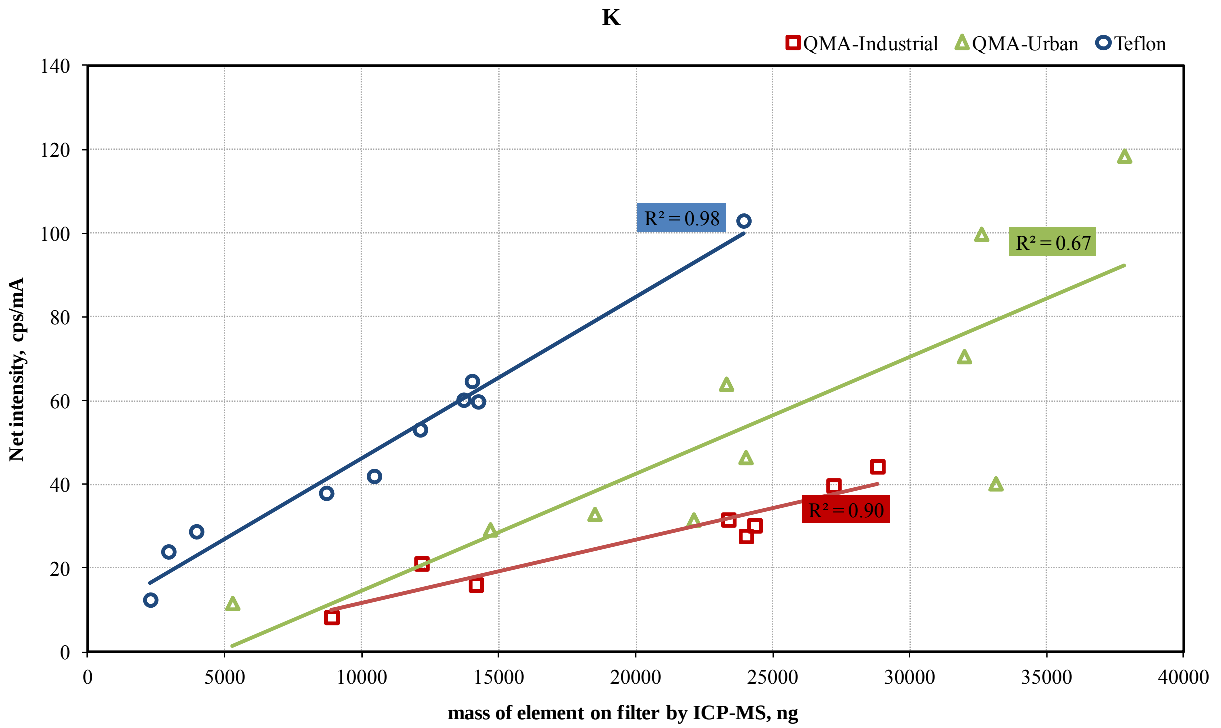
Finally, for Pb, Mn, Fe, Cu and Ti linear calibration by standards consisting of Teflon and QMA filters was enough accurate (deviations were less than 25%). It was found to be site and filter type independent. For Zn, linear calibration was found only independent of the type of filter at urban sites. However, for Ca, the filter type affected the results while no site effect could be evidenced for the QMA filters. On the opposite, site effect was evidenced for Al, Cr, Mg, K, As, Ni, Zn and V. For QMA, linear calibration with filters loaded at urban sites gave accurate results for As, Cu, Cr, Fe, Mn, Pb, V and Zn even if analyzing a sample collected at a different urban site. For QMA, linear calibration with filters of urban and industrial sites did not give satisfactory results for Ni and Al. For Teflon filters, the linear calibration gave satisfying results when quantifying filters of another urban site for Cr, Cu, Fe, Mg, Mn, Mo, Pb, Sr, Ti and V, only for filters of sampling sites of the same type as the one used for calibration. It was evidenced that Teflon filters are more appropriate than QMA filters to analyze elements by EDXRF. The main findings supporting this conclusion were: higher R^2 and lower U_r for Teflon than QMA filters. Moreover, the quantification of filters loaded at an urban sampling site different than the one used for calibration was more successful with Teflon filters compared to quartz filters. More tests in different sites of calibration are required to check the site effect on Teflon filters. Standardless EDXRF analysis was found to be more efficient than linear calibration for the quantification of trace elements. First, this calibration method is filter type and sampling site independent. Then for Teflon filters, standardless EDXRF analysis showed better results than linear calibration except for Al, Pb, Sr, As, Co and V. For QMA filters, standardless EDXRF analysis showed better results than linear calibration except for Cr, Zn and V. Consequently, in the rest of this report, only standardless EDXRF analysis will be considered both on Teflon and quartz filters.


Al
QMA-Industrial
QMA-Urban
Teflon
R² = 0.98
R² = 0.72
Net intensity, cps/mA
250
200
150
100
50
0
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
mass of element on filter by ICPMS, ng

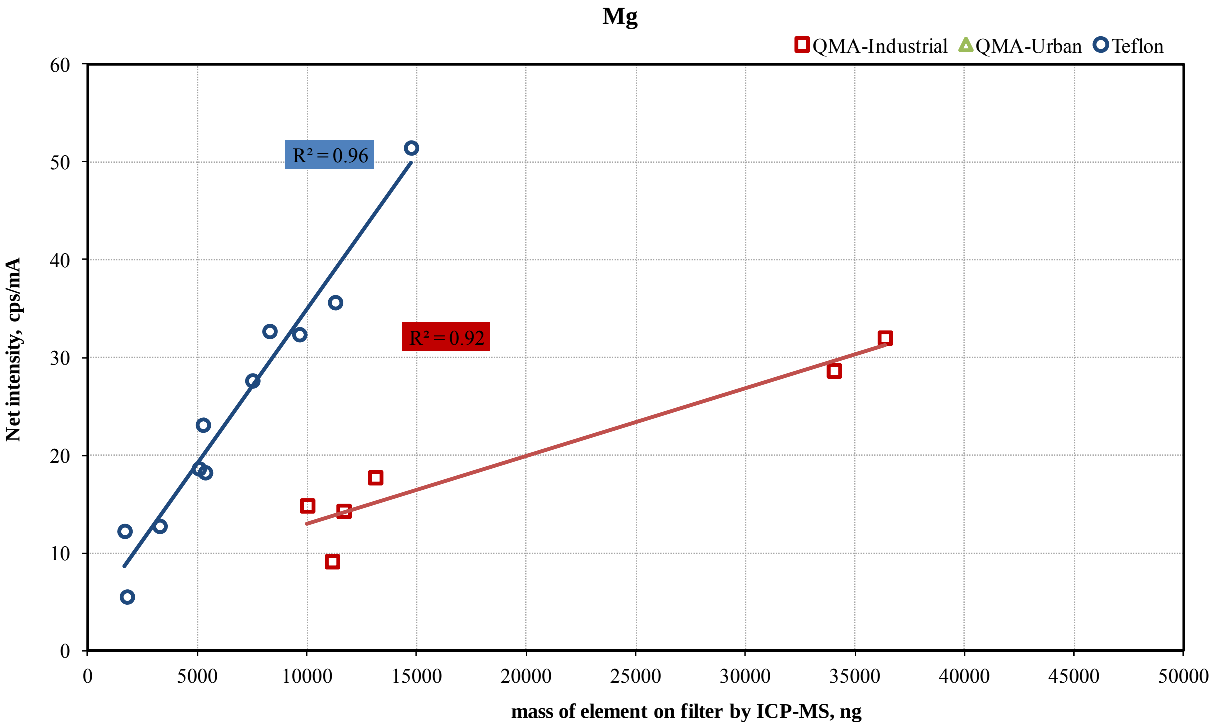

Ca
QMA-Industrial
QMA-Urban
Teflon
R² = 0.94
R² = 0.98
R² = 0.97
Net intensity, cps/mA
700
600
500
400
300
200
100
0
0
20000
40000
60000
80000
100000
120000
140000
160000
180000
200000
mass of element on filter by ICP-MS, ng

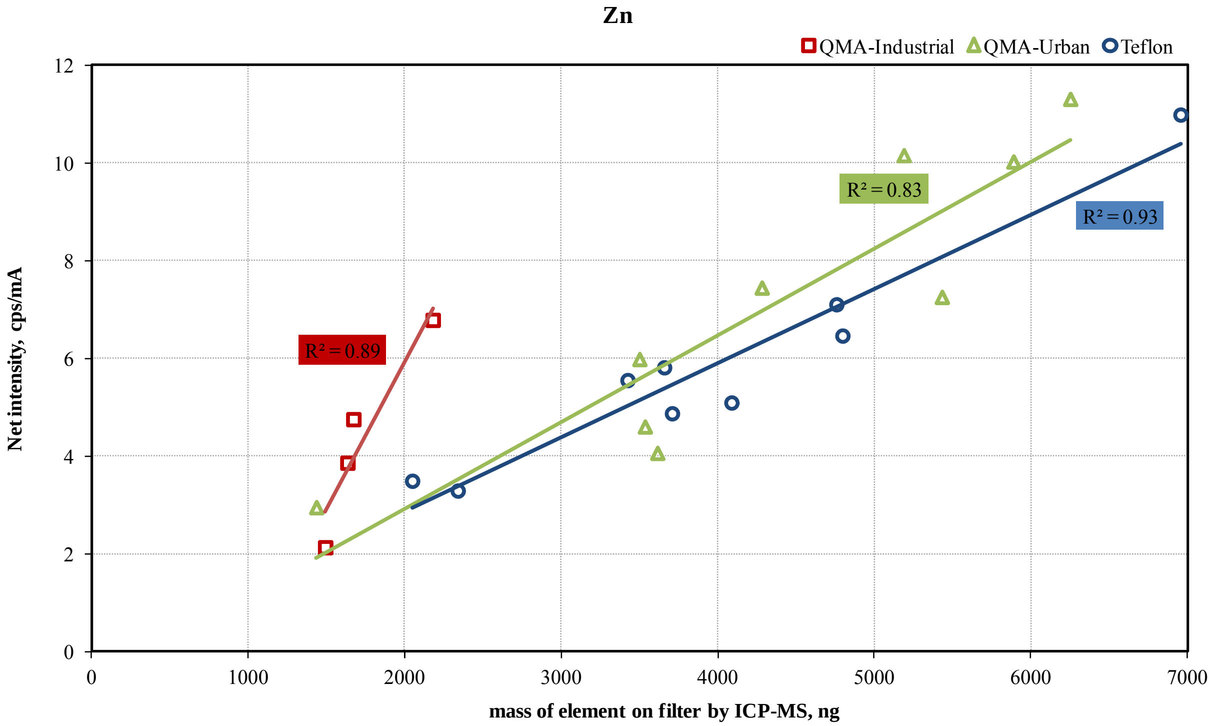

Fe

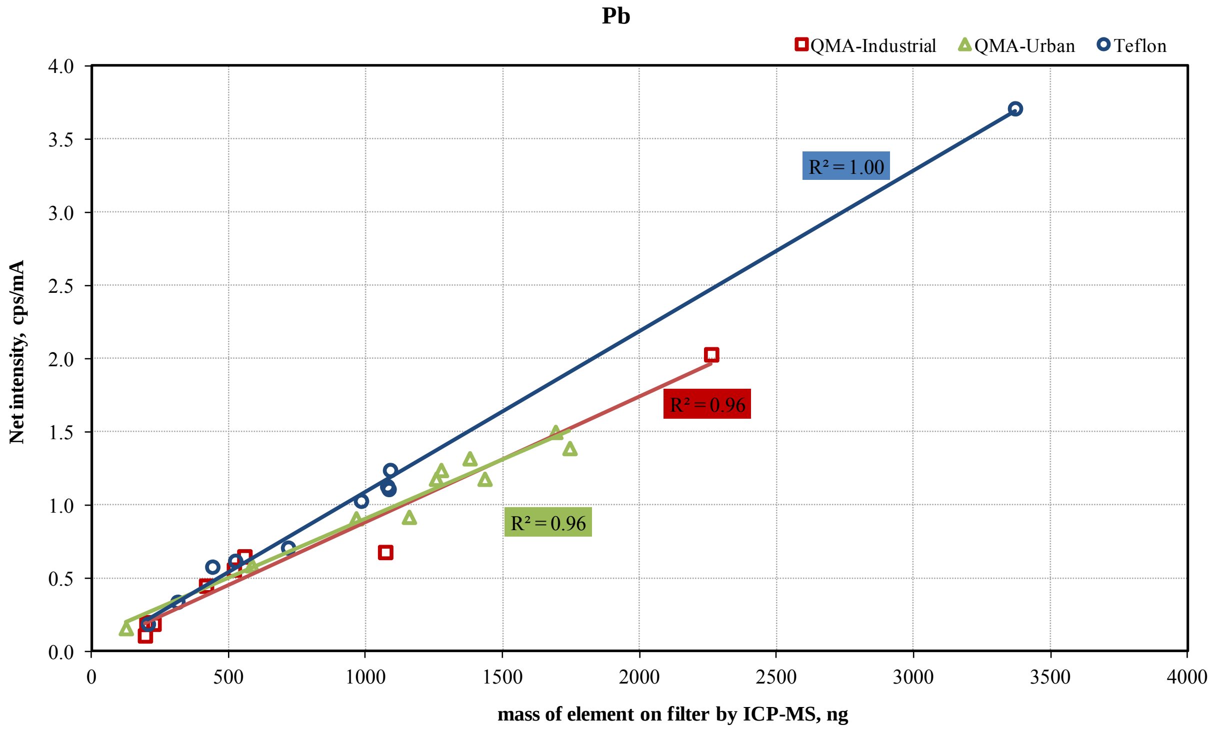
QMA-Industrial
QMA-Urban
Teflon
R² = 0.98
R² = 0.97
R² = 0.99
Net intensity, cps/mA
0
100
200
300
400
500
600
700
0
50000
100000
150000
200000
250000
300000
350000
mass of element on filter by ICP-MS, ng

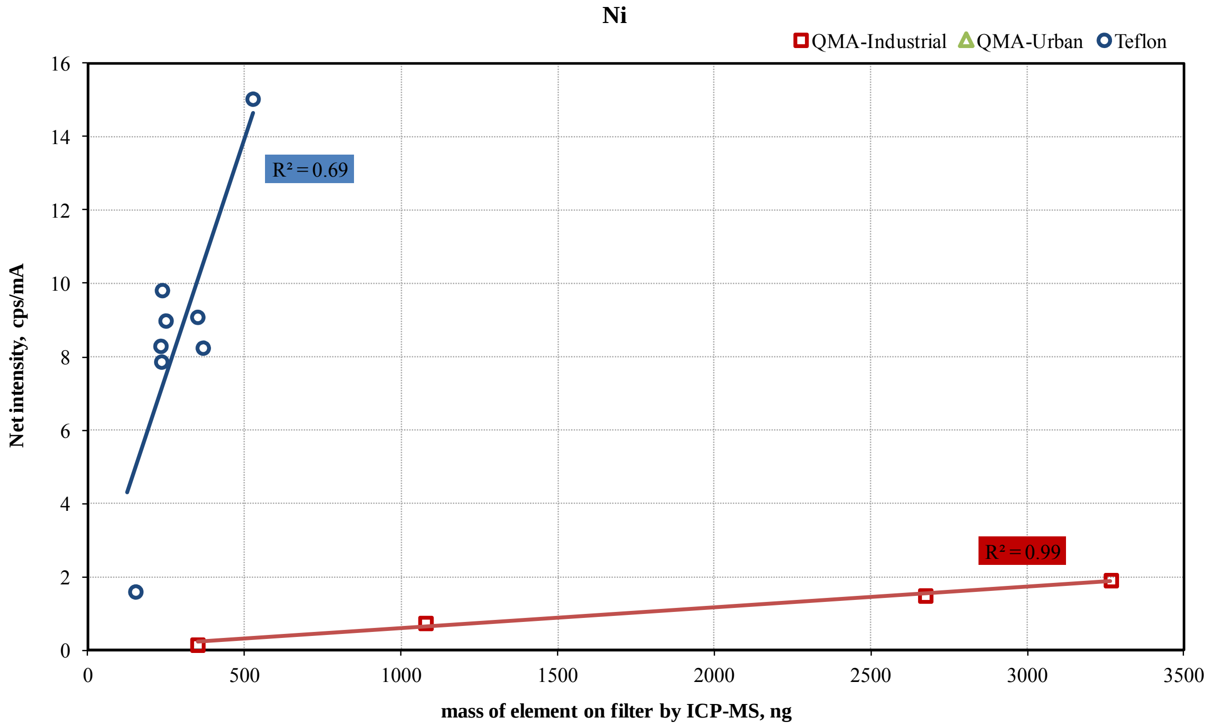

K

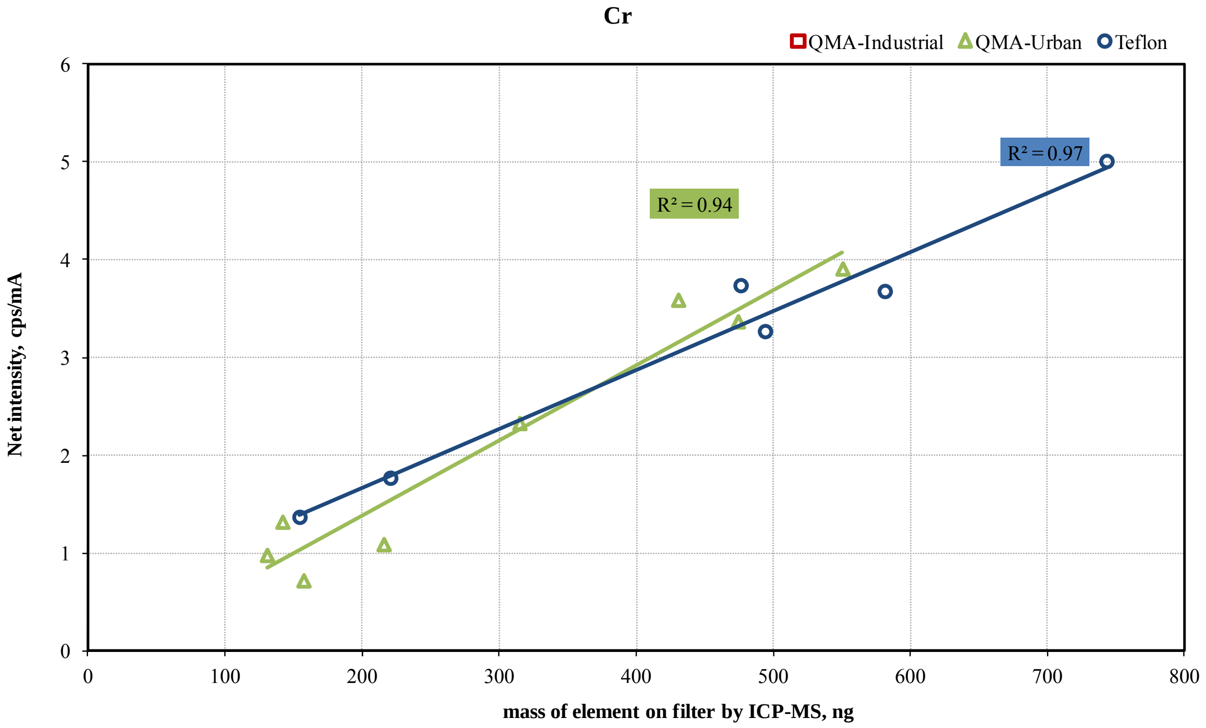
QMA-Industrial
QMA-Urban
Teflon
R² = 0.98
R² = 0.67
R² = 0.90
Net intensity, cps/mA
0
20
40
60
80
100
120
140
0
5000
10000
15000
20000
25000
30000
35000
40000
mass of element on filter by ICP-MS, ng

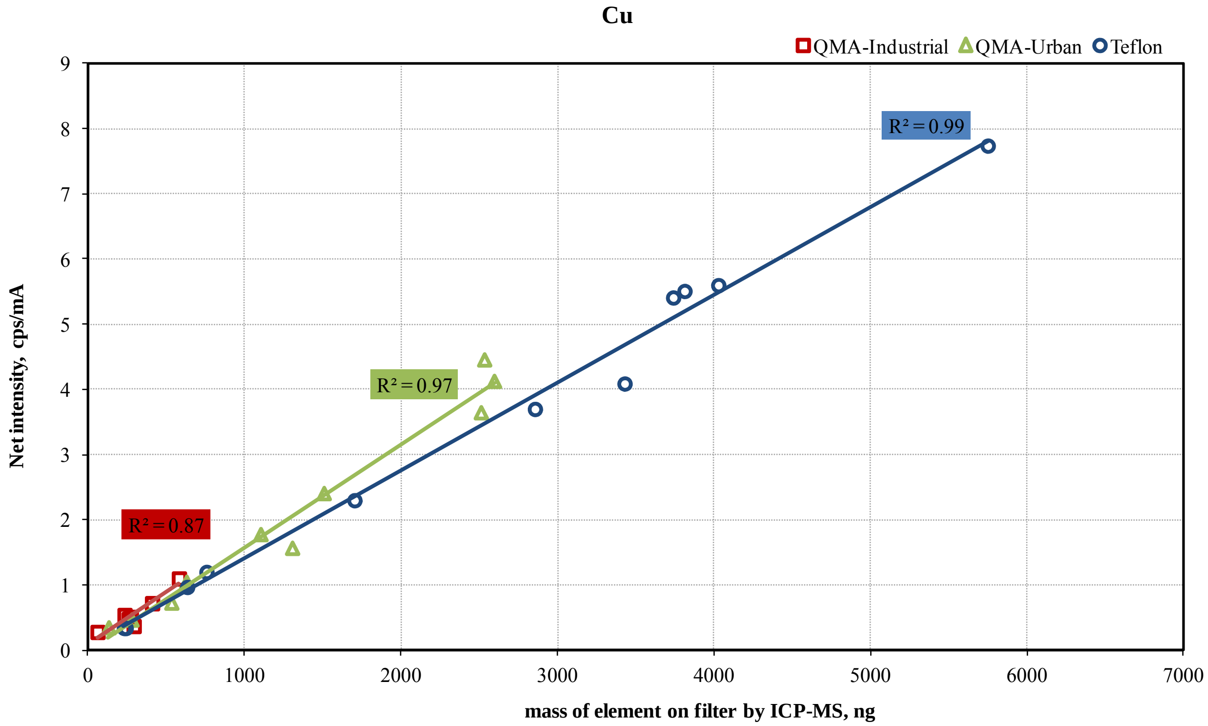

Mg
QMA-Industrial
QMA-Urban
Teflon
R² = 0.96
R² = 0.92
Net intensity, cps/mA
0
10
20
30
40
50
60
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
mass of element on filter by ICP-MS, ng

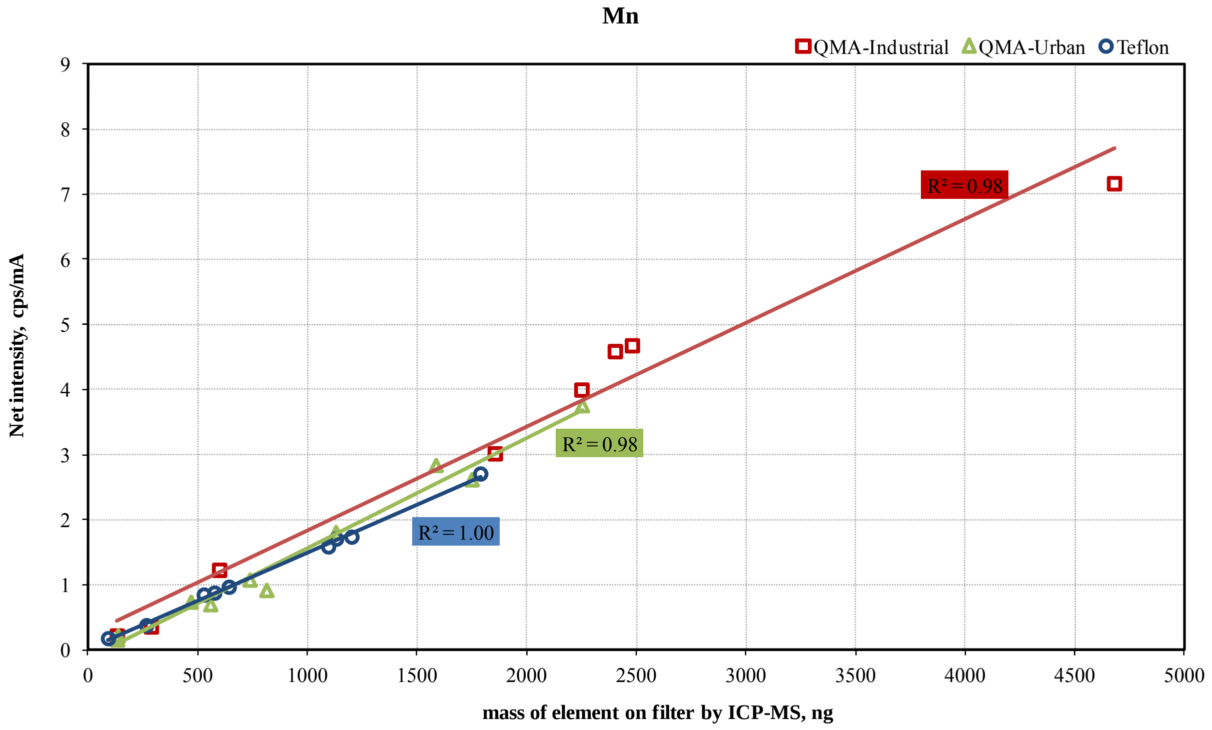

Zn
QMA-Industrial
QMA-Urban
Teflon
R² = 0.89
R² = 0.83
R² = 0.93
Net intensity, cps/mA
0
2
4
6
8
10
12
0
1000
2000
3000
4000
5000
6000
7000
mass of element on filter by ICP-MS, ng

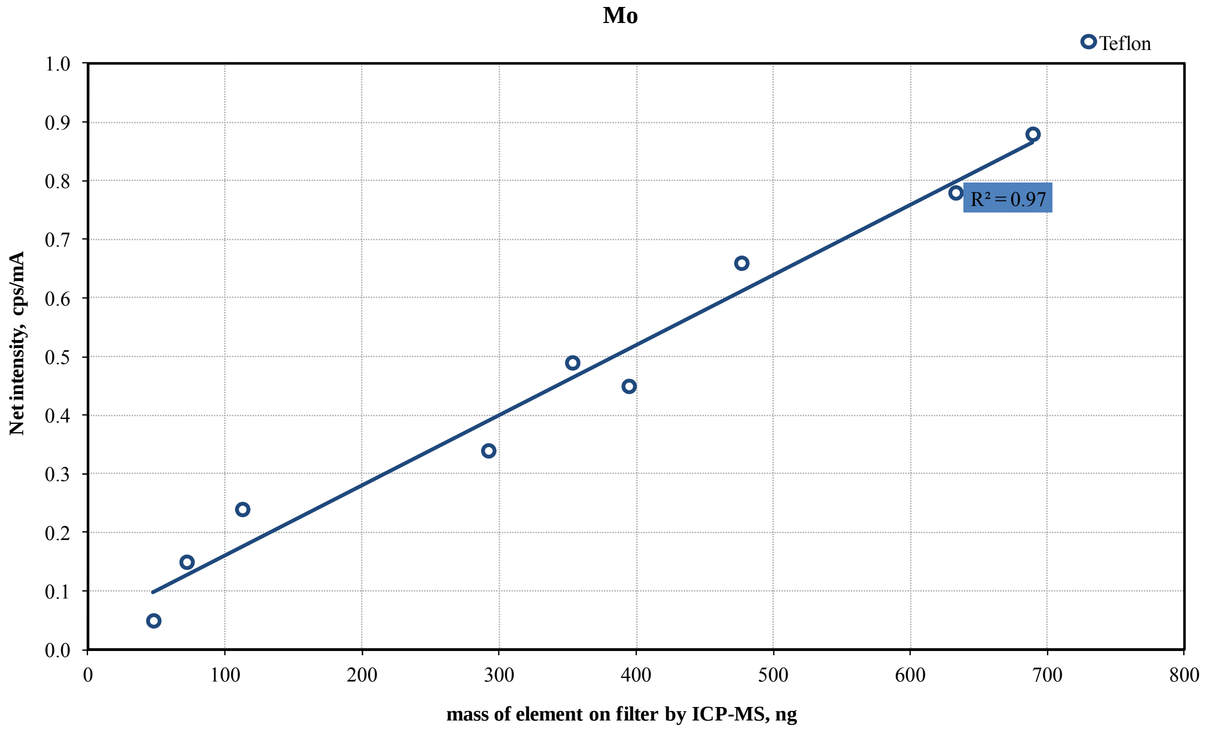

Pb
QMA-Industrial
QMA-Urban
Teflon
R² = 1.00
R² = 0.96
R² = 0.96
Net intensity, cps/mA
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
500
1000
1500
2000
2500
3000
3500
4000
mass of element on filter by ICP-MS, ng

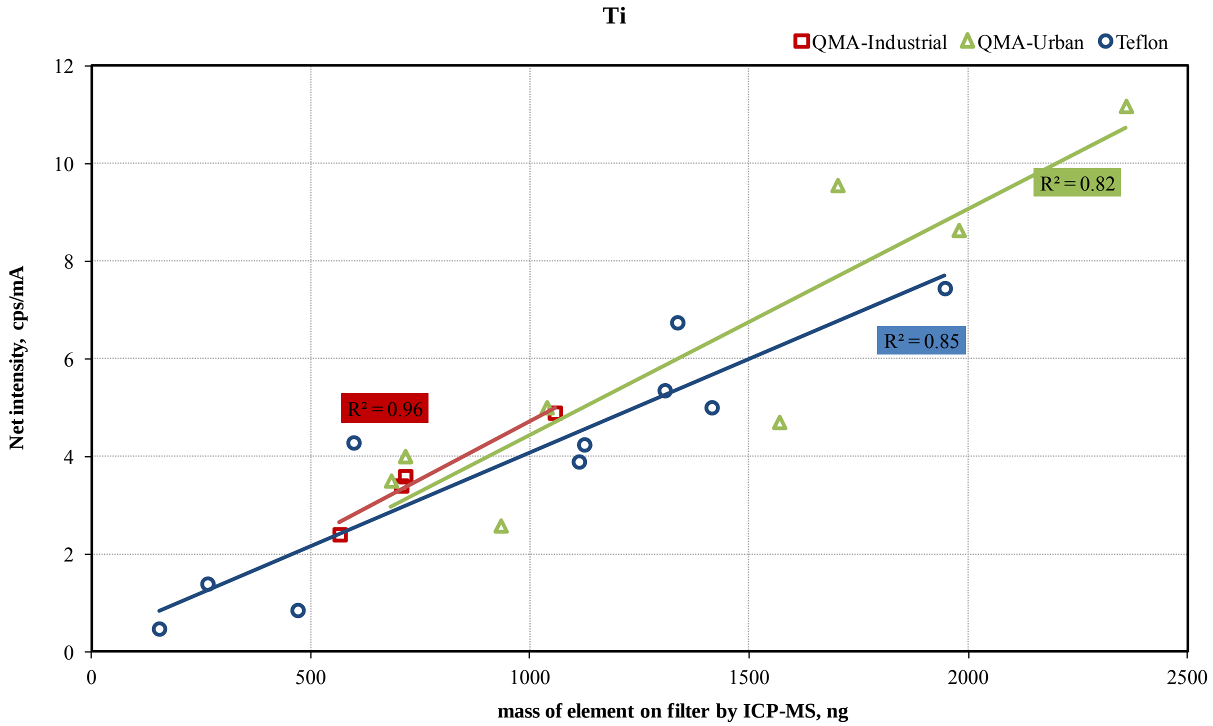

Ni
QMA-Industrial
QMA-Urban
Teflon
R² = 0.69
R² = 0.99
Net intensity, cps/mA
0
2
4
6
8
10
12
14
16
0
500
1000
1500
2000
2500
3000
3500
mass of element on filter by ICP-MS, ng

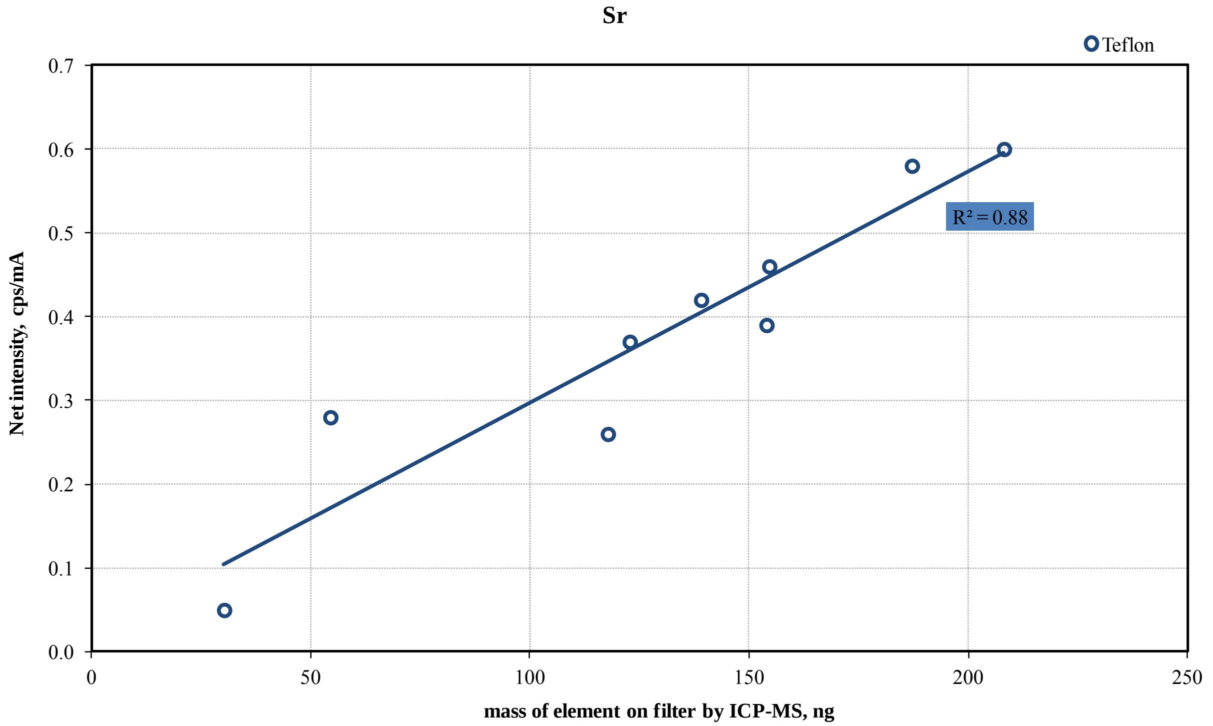

Cr
QMA-Industrial
QMA-Urban
Teflon
R² = 0.97
R² = 0.94
Net intensity, cps/mA
0
1
2
3
4
5
6
0
100
200
300
400
500
600
700
800
mass of element on filter by ICP-MS, ng

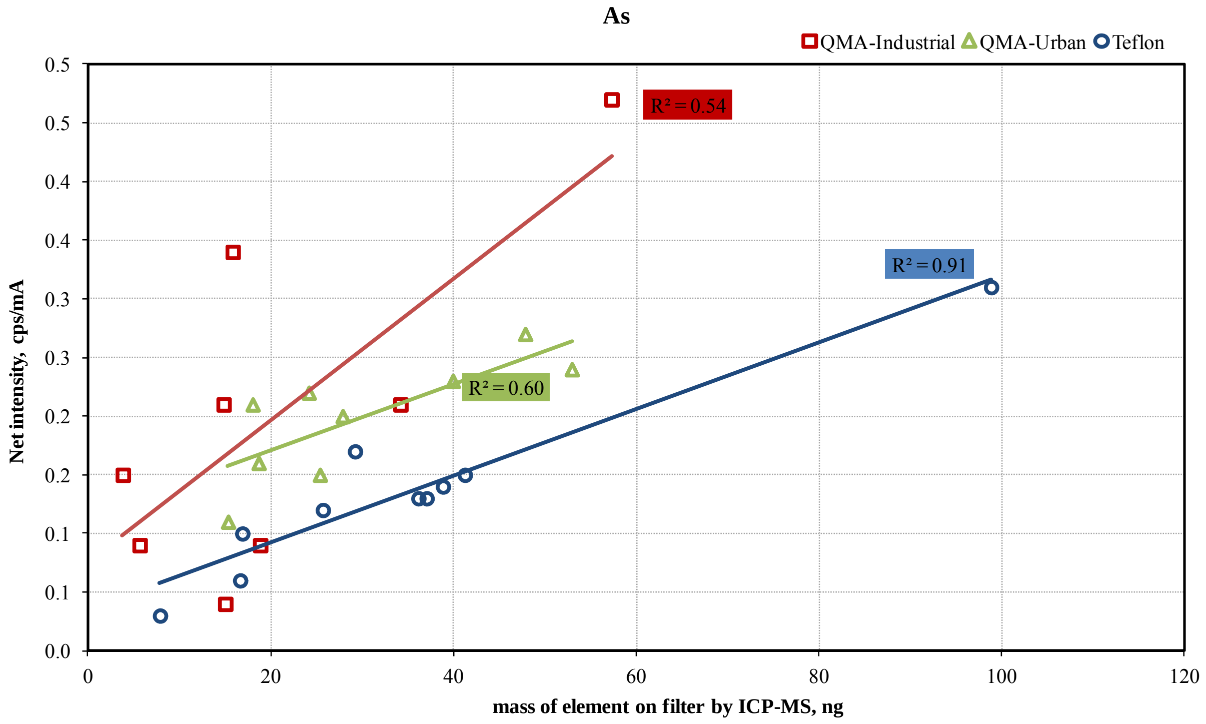

Cu
QMA-Industrial
QMA-Urban
Teflon
R² = 0.99
R² = 0.97
R² = 0.87
Net intensity, cps/mA
0
1
2
3
4
5
6
7
8
9
0
1000
2000
3000
4000
5000
6000
7000
mass of element on filter by ICP-MS, ng

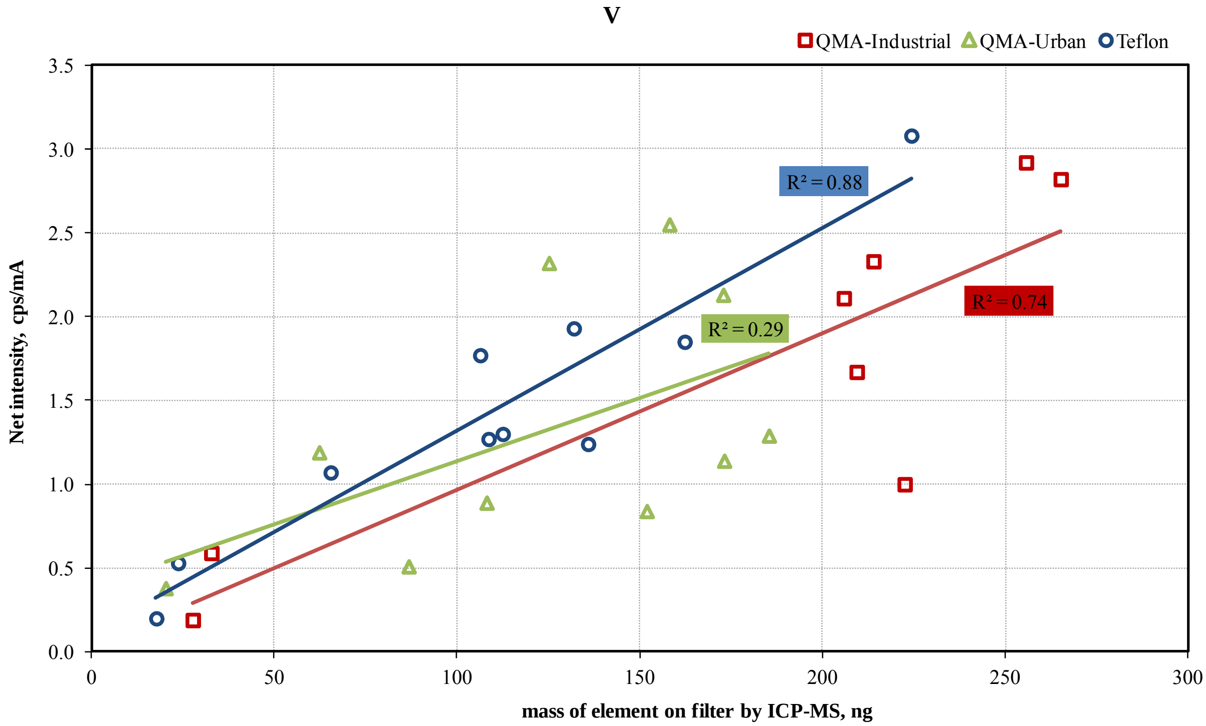

Mn
QMA-Industrial
QMA-Urban
Teflon
R² = 0.98
R² = 0.98
R² = 1.00
Net intensity, cps/mA
9
8
7
6
5
4
3
2
1
0
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
mass of element on filter by ICP-MS, ng


Mo
Teflon
R² = 0.97
Net intensity, cps/mA
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
800
mass of element on filter by ICP-MS, ng


Ti
QMA-Industrial
QMA-Urban
Teflon
R² = 0.82
R² = 0.85
R² = 0.96
Net intensity, cps/mA
mass of element on filter by ICP-MS, ng
0
2
4
6
8
10
12
0
500
1000
1500
2000
2500


Sr
Teflon
R² = 0.88
Net intensity, cps/mA
mass of element on filter by ICP-MS, ng
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
50
100
150
200
250


As
QMA-Industrial
QMA-Urban
Teflon
R² = 0.54
R² = 0.91
R² = 0.60
Net intensity, cps/mA
0.0
0.1
0.1
0.2
0.2
0.3
0.3
0.4
0.4
0.5
0.5
0
20
40
60
80
100
120
mass of element on filter by ICP-MS, ng


V
QMA-Industrial
QMA-Urban
Teflon
R² = 0.88
R² = 0.74
R² = 0.29
Net intensity, cps/mA
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0
50
100
150
200
250
300
mass of element on filter by ICP-MS, ng

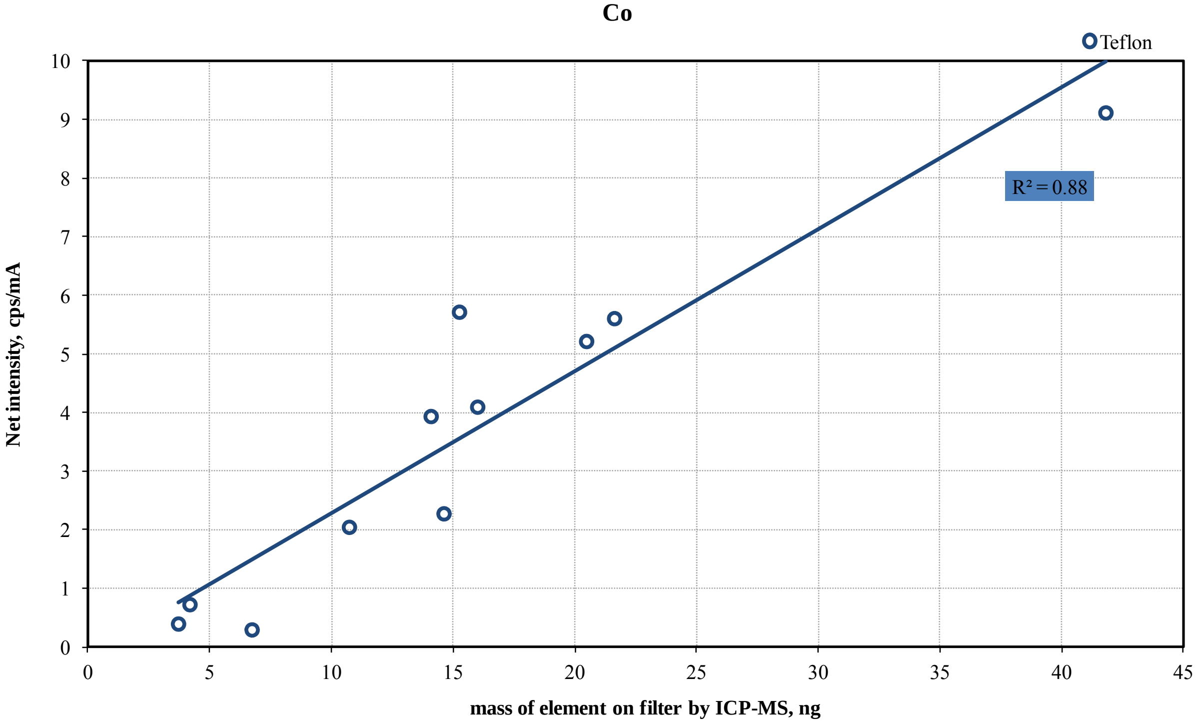


Figure 1. Linear calibration for Teflon filters at urban site and for QMA at urban and industrial sites

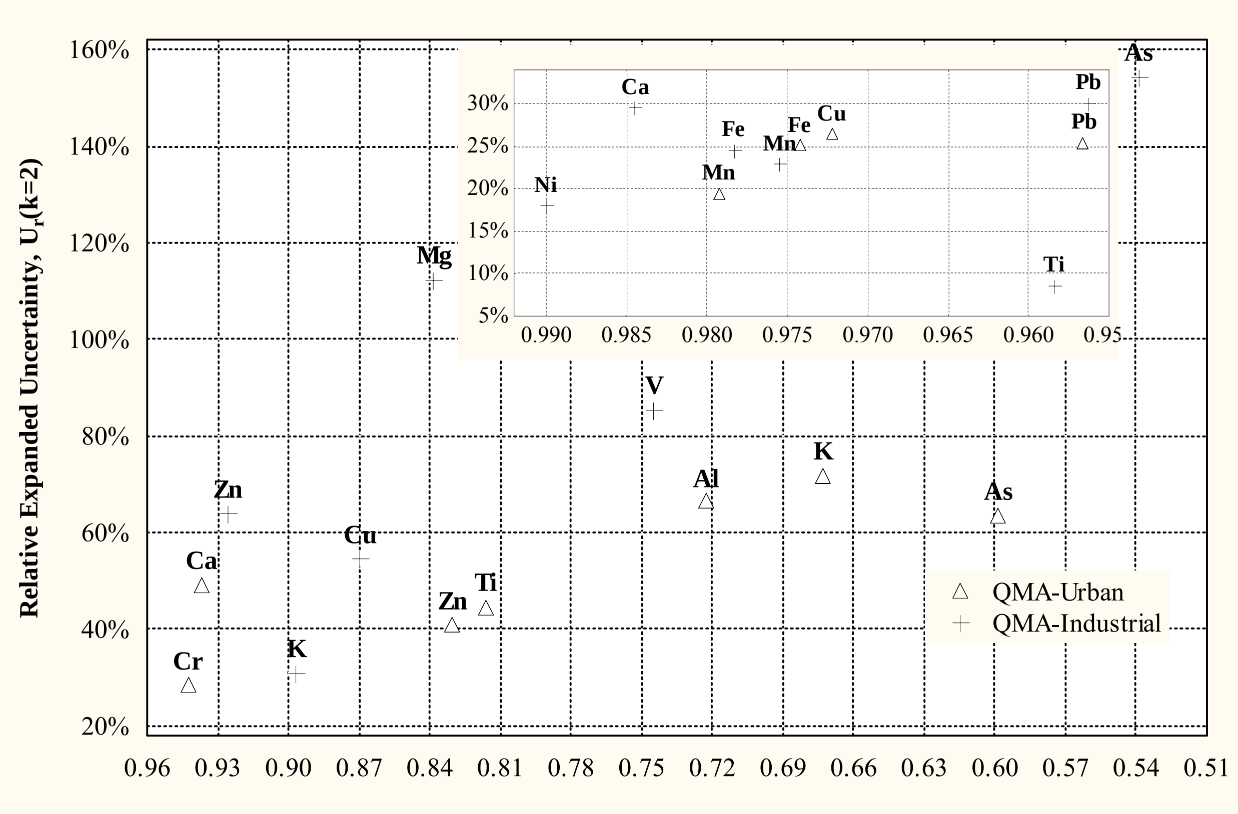


Figure 2: Relative expanded uncertainty (U_r, k=2) estimated using the lack of fit of the linear calibration function at the central point of each elemental mass range versus R^2 for QMA filters at urban and industrial sites. The elements with high R^2 were presented in the inner figure

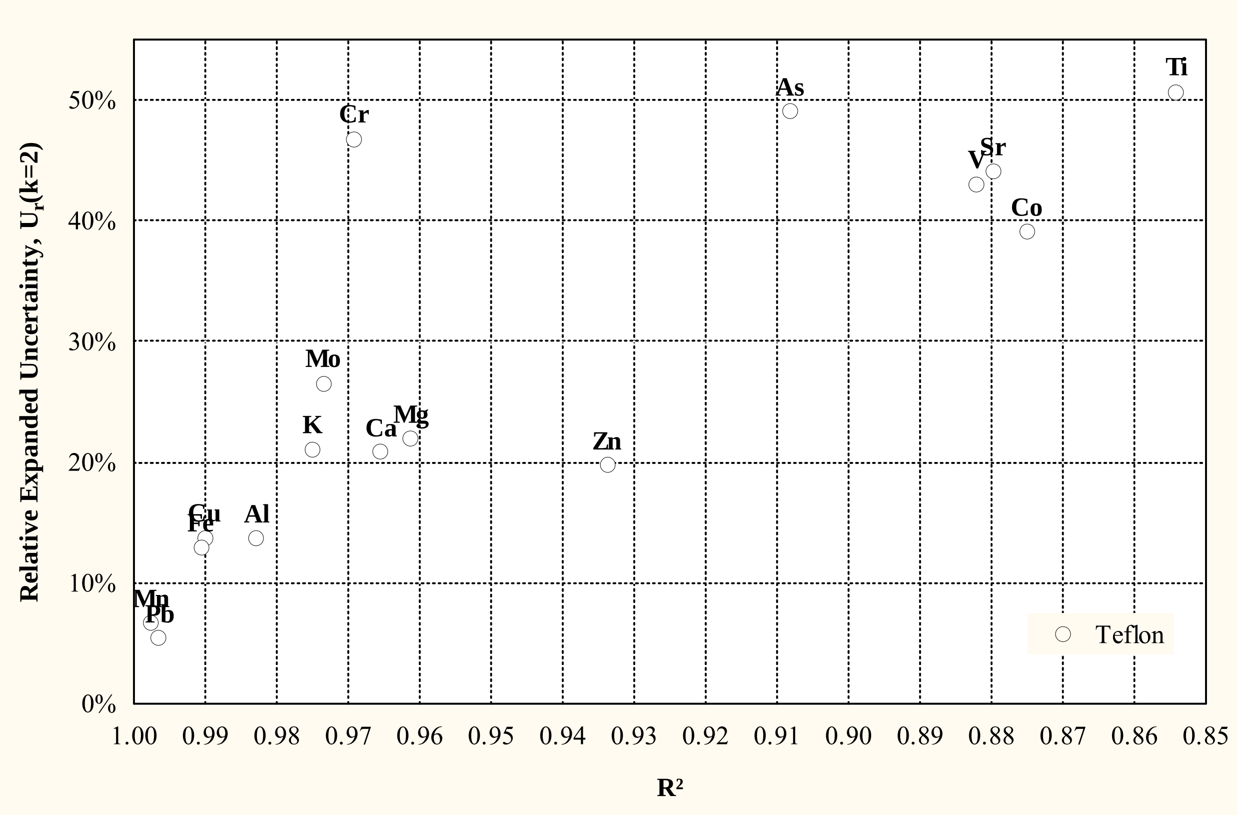
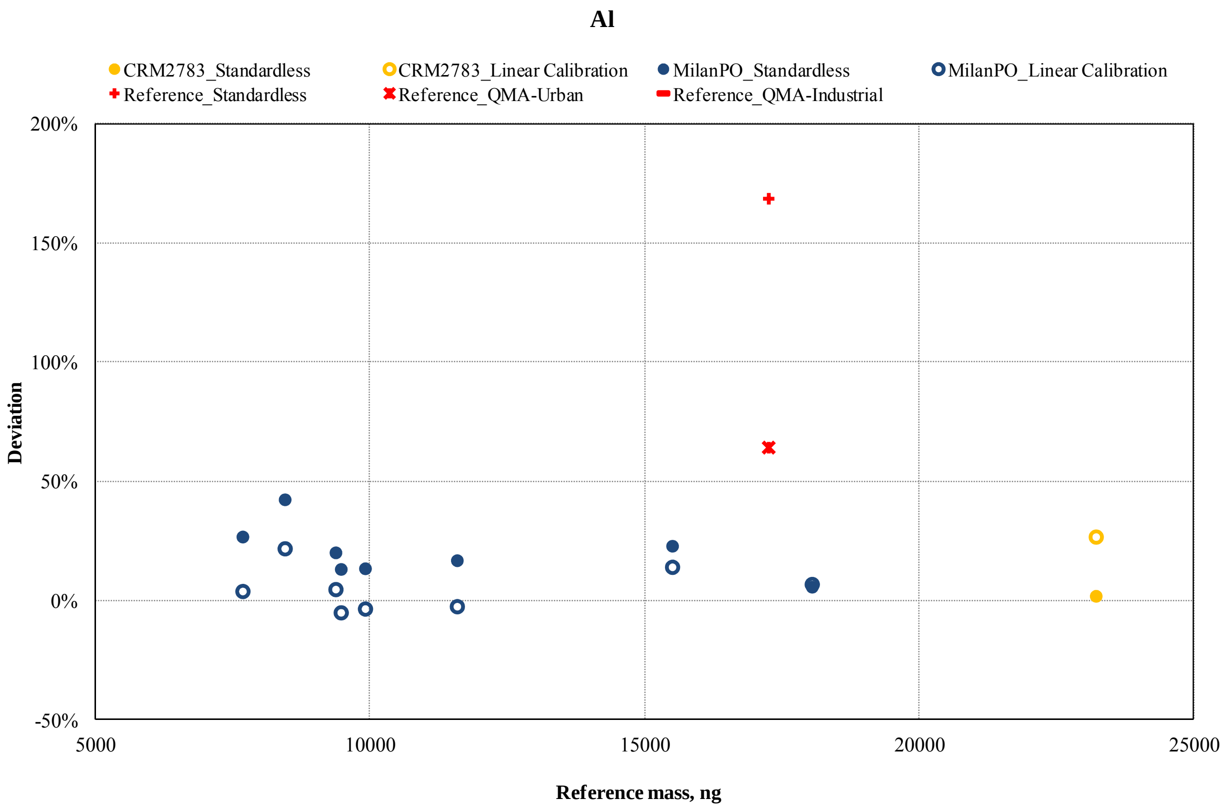
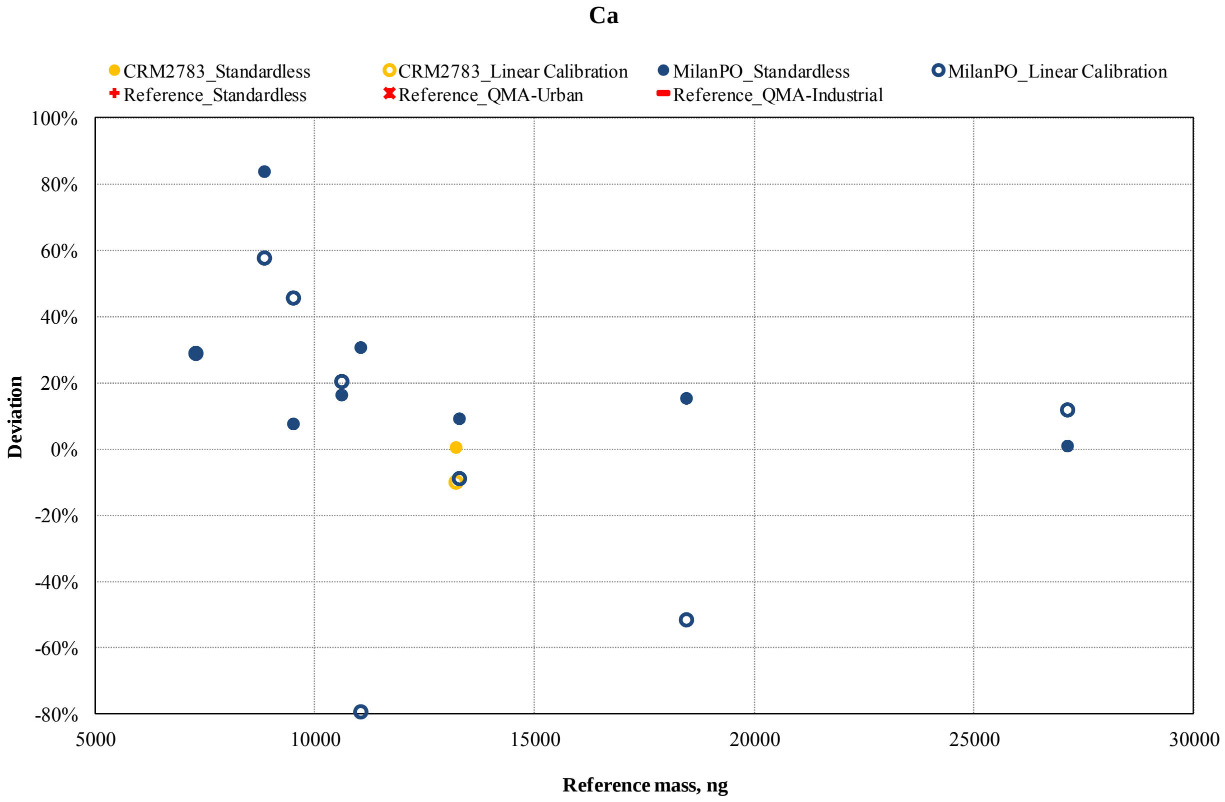
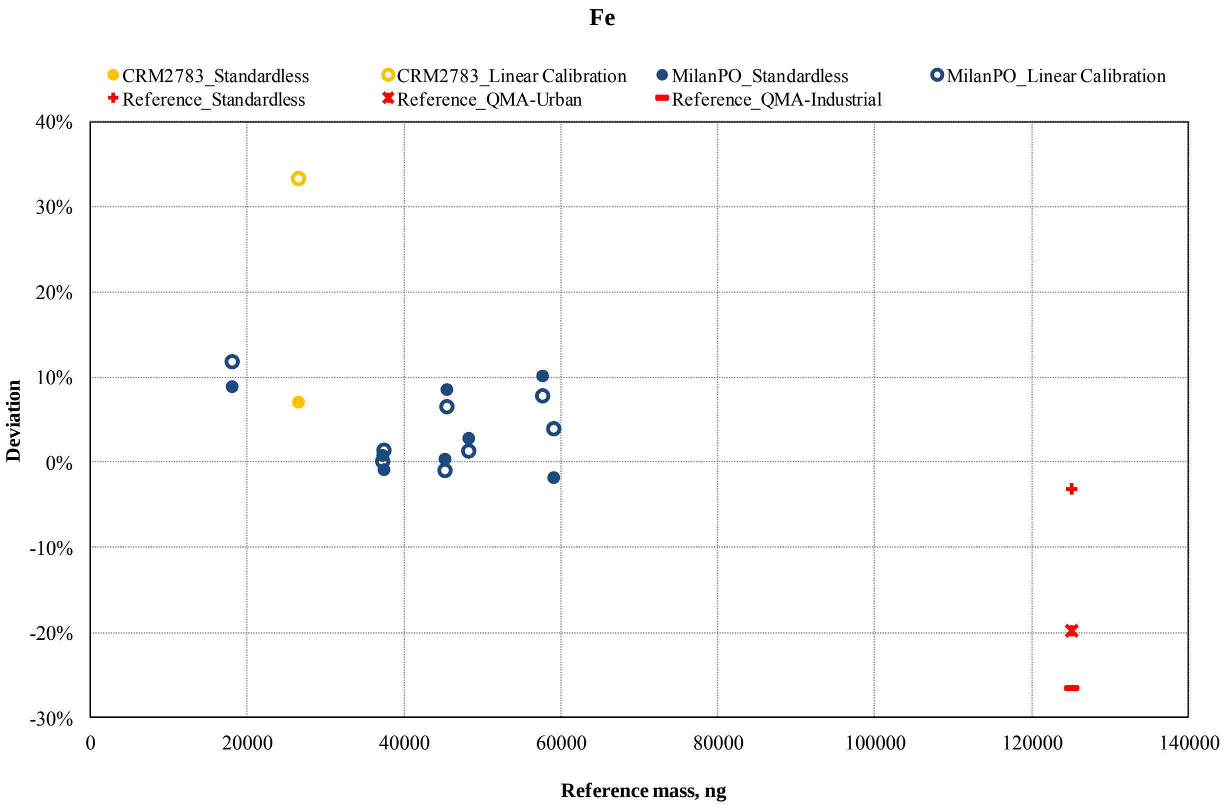
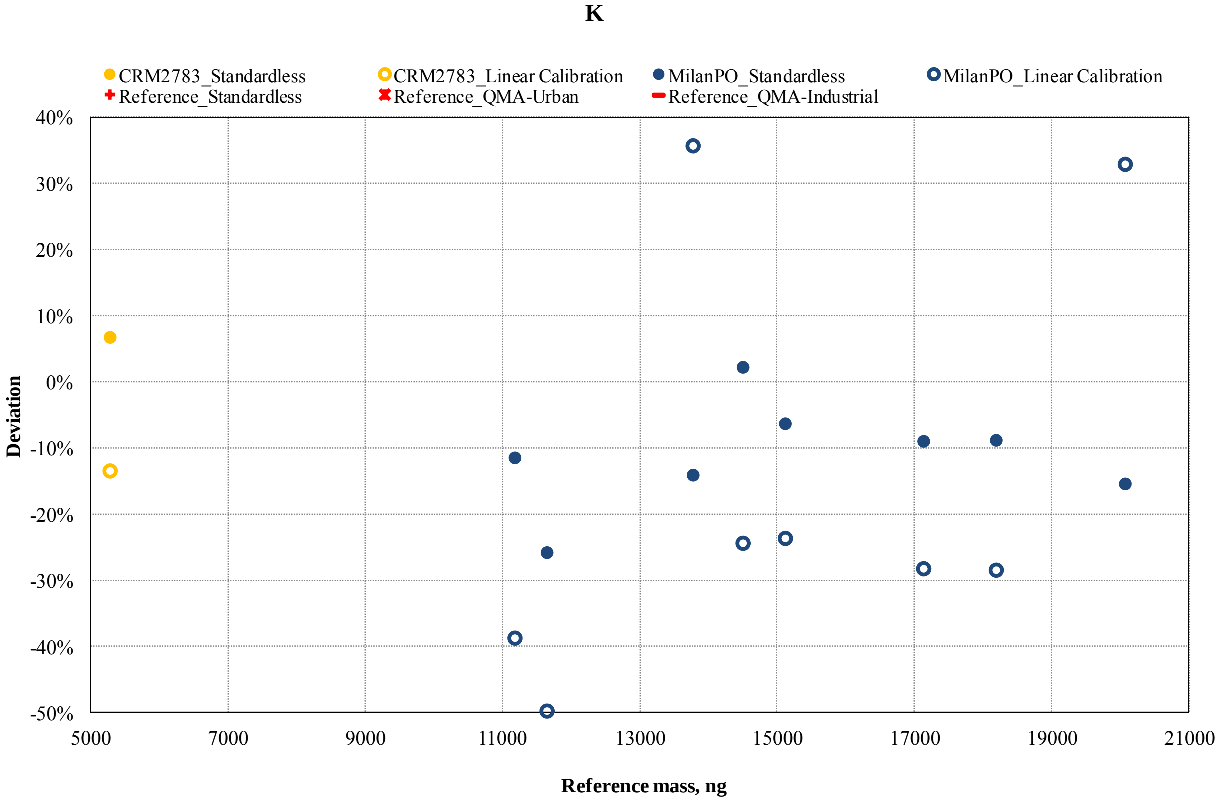


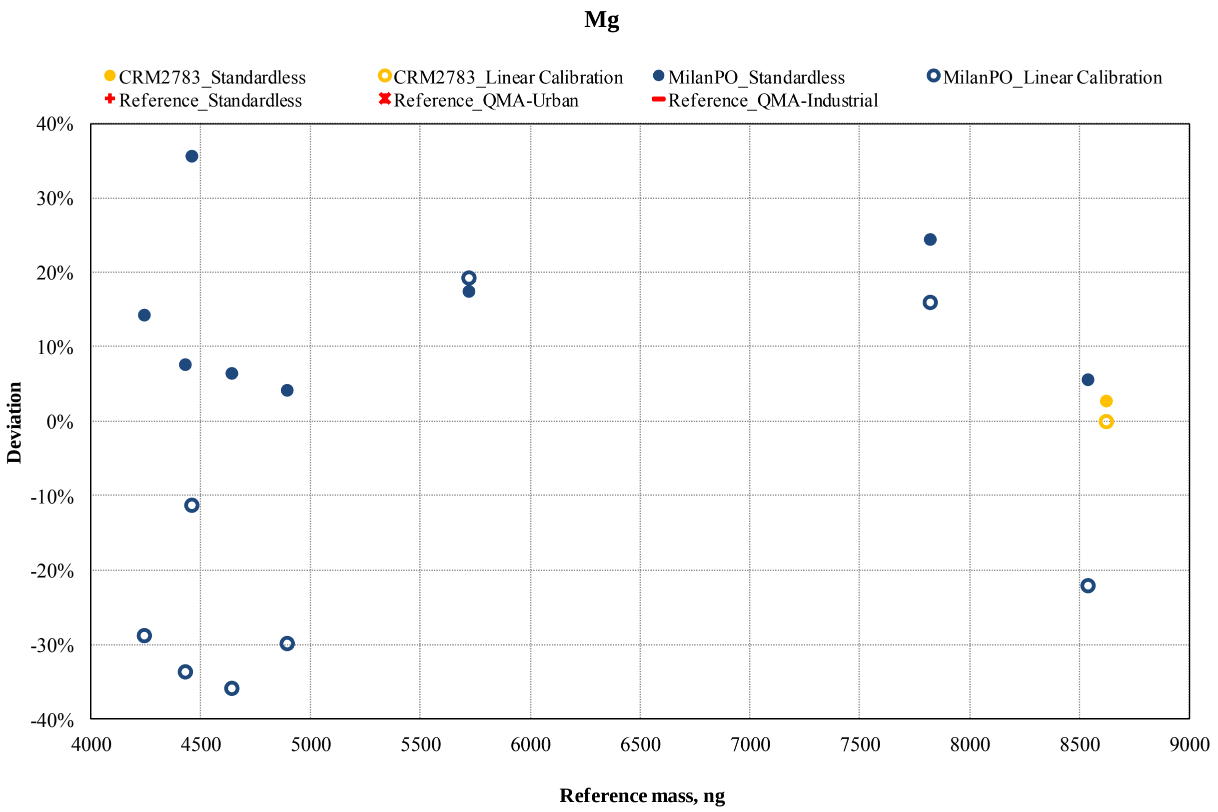
Figure 3: Relative expanded uncertainty (U_r, k=2) estimated using the lack of fit of the linear calibration function at the central point of each elemental mass range versus R^2 for Teflon filters. Ni (0.57, 67%) was excluded for better view

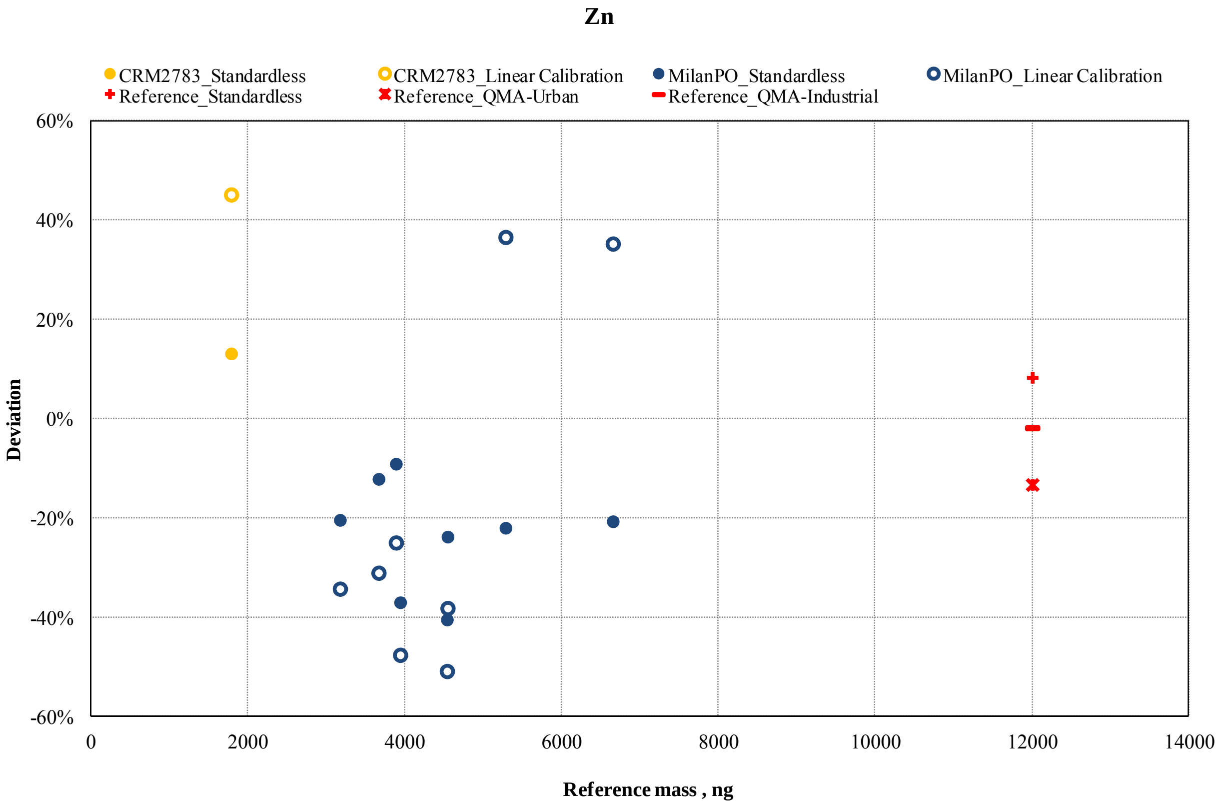

Al
CRM2783_Standardless
CRM2783_Linear Calibration
MilanPO_Standardless
MilanPO_Linear Calibration
Reference_Standardless
Reference_QMA-Urban
Reference_QMA-Industrial
Deviation
200%
150%
100%
50%
0%
-50%
5000
10000
15000
20000
25000
Reference mass, ng

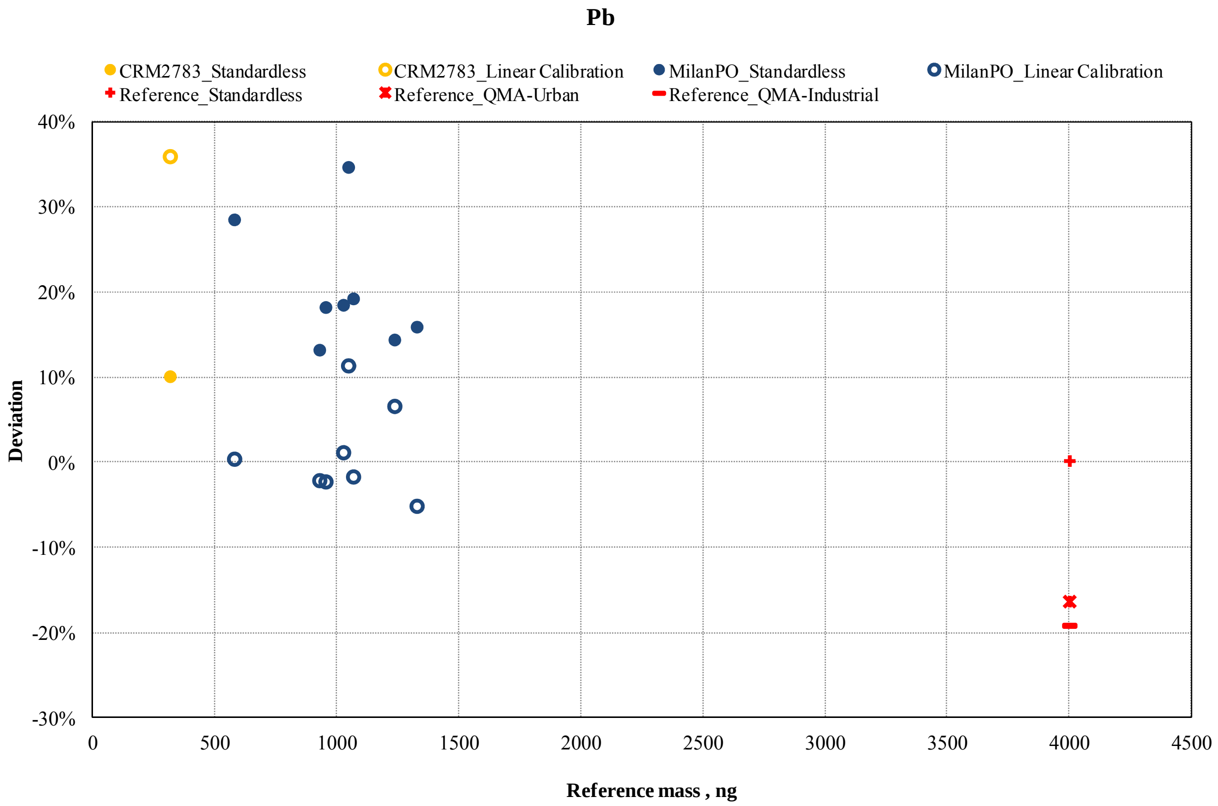

Ca
CRM2783_Standardless
CRM2783_Linear Calibration
MilanPO_Standardless
MilanPO_Linear Calibration
Reference_Standardless
Reference_QMA-Urban
Reference_QMA-Industrial
Deviation
100%
80%
60%
40%
20%
0%
-20%
-40%
-60%
-80%
5000
10000
15000
20000
25000
30000
Reference mass, ng

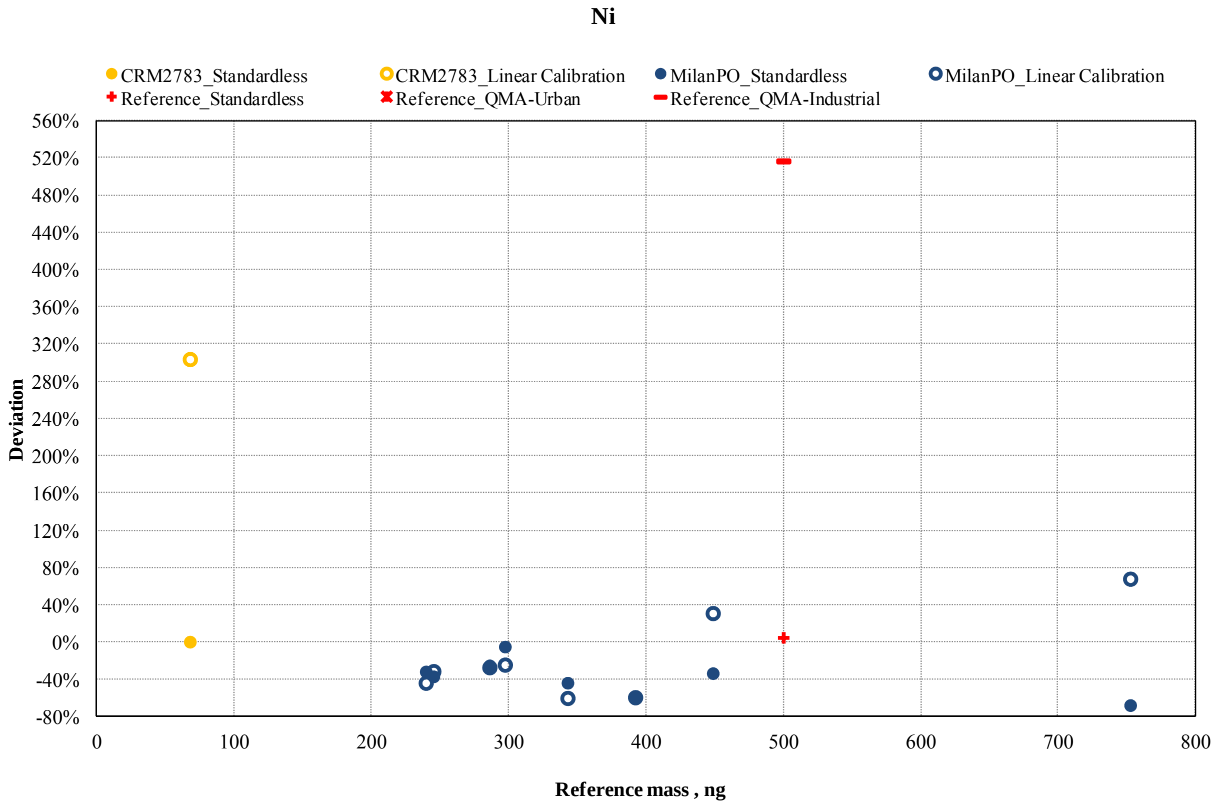

Fe
● CRM2783_Standardless
○ CRM2783_Linear Calibration
● MilanPO_Standardless
○ MilanPO_Linear Calibration
✚ Reference_Standardless
✖ Reference_QMA-Urban
▬ Reference_QMA-Industrial
Deviation
40%
30%
20%
10%
0%
-10%
-20%
-30%
0
20000
40000
60000
80000
100000
120000
140000
Reference mass, ng

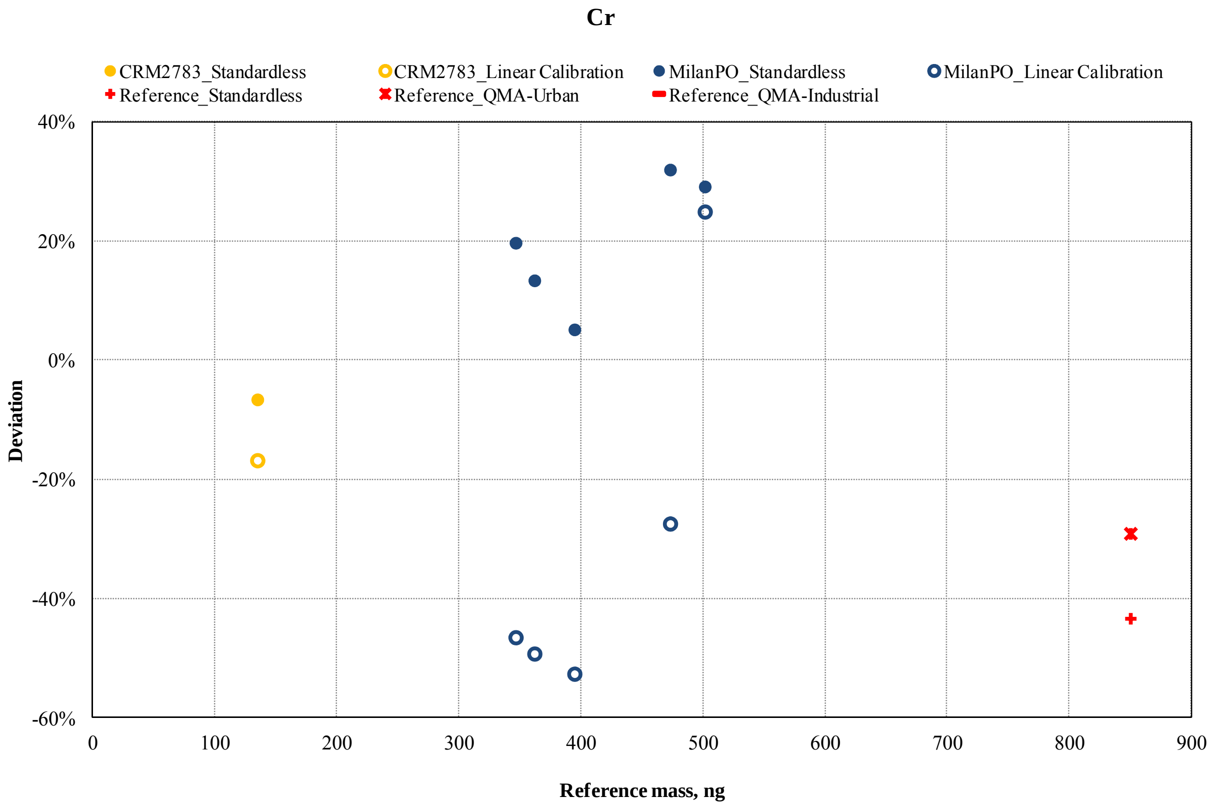

K
● CRM2783_Standardless
○ CRM2783_Linear Calibration
● MilanPO_Standardless
○ MilanPO_Linear Calibration
✚ Reference_Standardless
✖ Reference_QMA-Urban
▬ Reference_QMA-Industrial
Deviation
40%
30%
20%
10%
0%
-10%
-20%
-30%
-40%
-50%
5000
7000
9000
11000
13000
15000
17000
19000
21000
Reference mass, ng

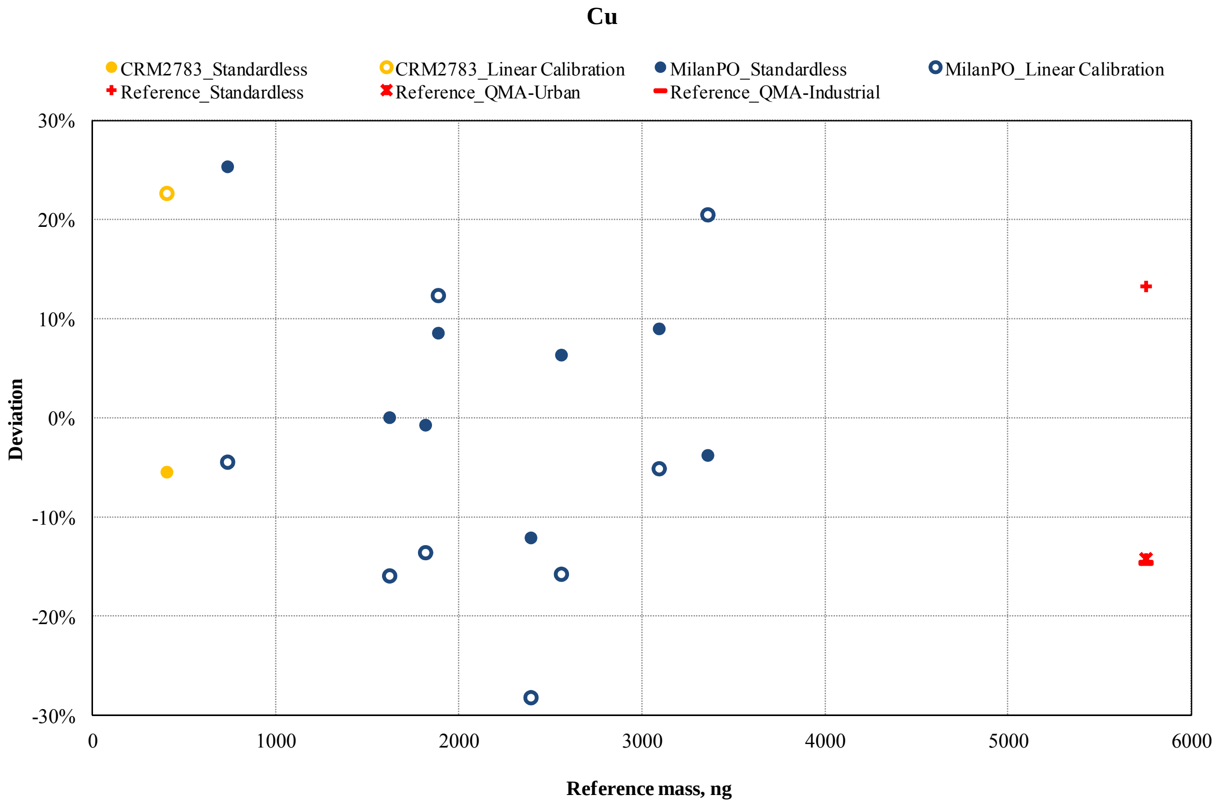

Mg
CRM2783_Standardless
CRM2783_Linear Calibration
MilanPO_Standardless
MilanPO_Linear Calibration
Reference_Standardless
Reference_QMA-Urban
Reference_QMA-Industrial
40%
30%
20%
10%
0%
-10%
-20%
-30%
-40%
Deviation
4000
4500
5000
5500
6000
6500
7000
7500
8000
8500
9000
Reference mass, ng

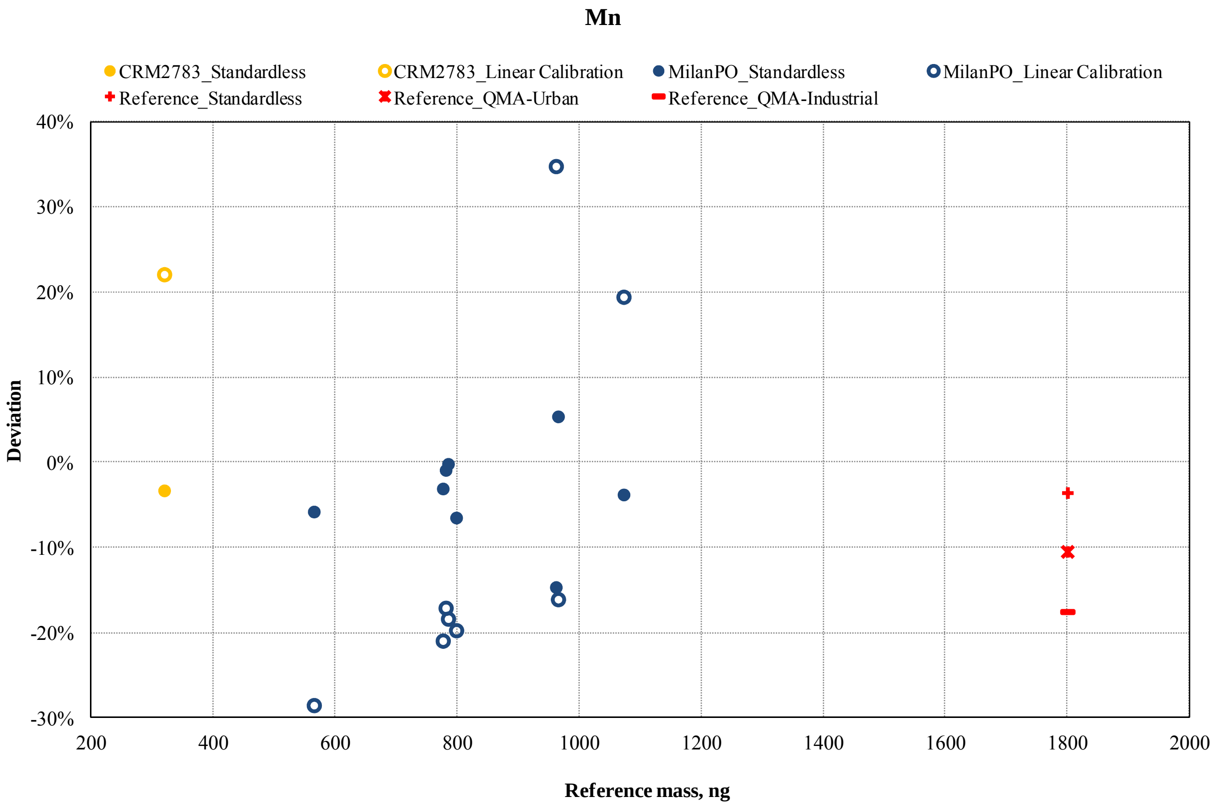

Zn
CRM2783_Standardless
CRM2783_Linear Calibration
MilanPO_Standardless
MilanPO_Linear Calibration
Reference_Standardless
Reference_QMA-Urban
Reference_QMA-Industrial
60%
40%
20%
0%
-20%
-40%
-60%
Deviation
0
2000
4000
6000
8000
10000
12000
14000
Reference mass , ng

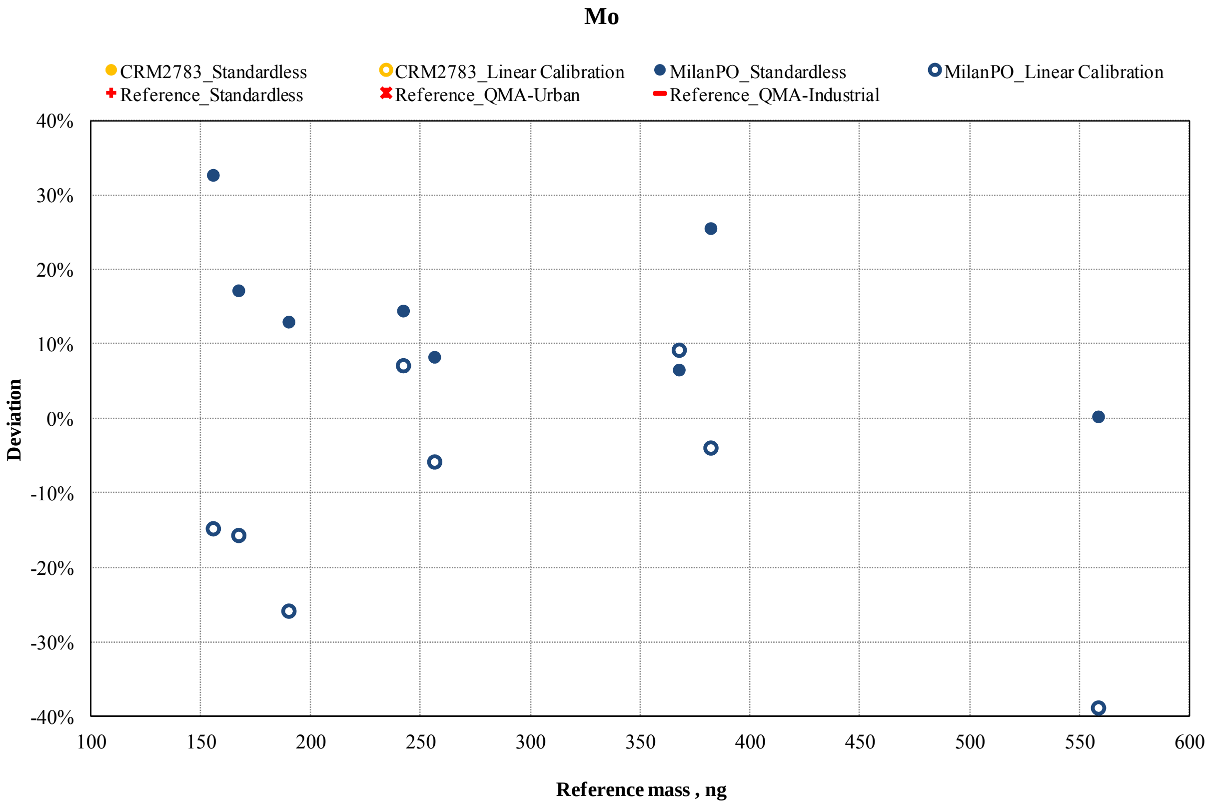

Pb
● CRM2783_Standardless
○ CRM2783_Linear Calibration
● MilanPO_Standardless
○ MilanPO_Linear Calibration
✚ Reference_Standardless
✖ Reference_QMA-Urban
▬ Reference_QMA-Industrial
Deviation
40%
30%
20%
10%
0%
-10%
-20%
-30%
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Reference mass , ng

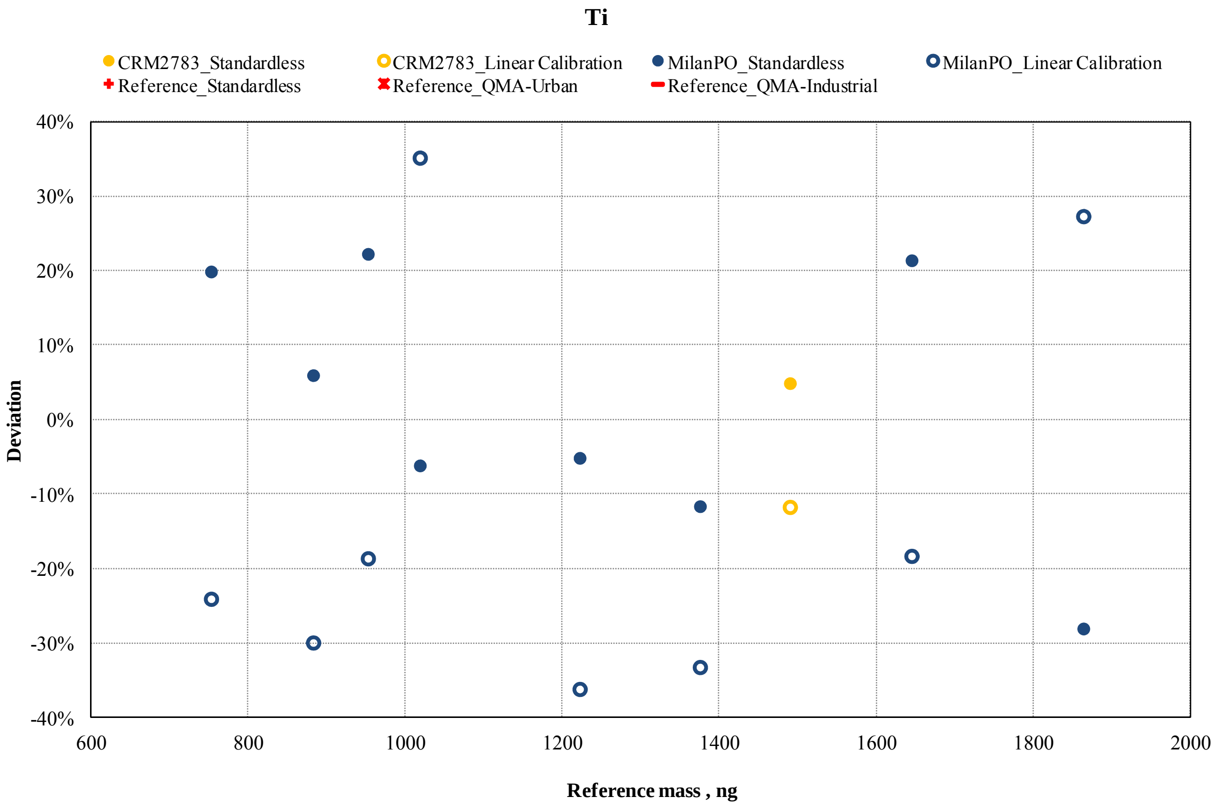

Ni
● CRM2783_Standardless
○ CRM2783_Linear Calibration
● MilanPO_Standardless
○ MilanPO_Linear Calibration
✚ Reference_Standardless
✖ Reference_QMA-Urban
▬ Reference_QMA-Industrial
Deviation
560%
520%
480%
440%
400%
360%
320%
280%
240%
200%
160%
120%
80%
40%
0%
-40%
-80%
0
100
200
300
400
500
600
700
800
Reference mass , ng

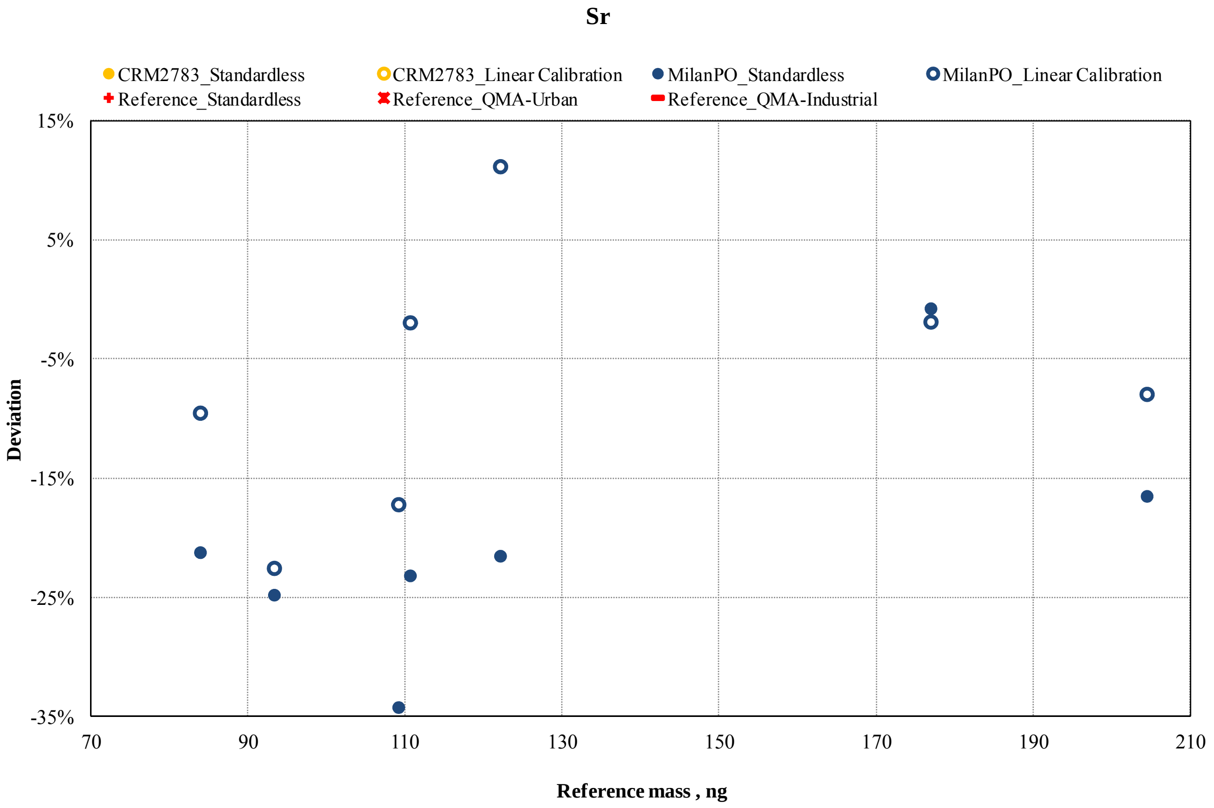

Cr
CRM2783_Standardless
CRM2783_Linear Calibration
MilanPO_Standardless
MilanPO_Linear Calibration
Reference_Standardless
Reference_QMA-Urban
Reference_QMA-Industrial
40%
20%
0%
-20%
-40%
-60%
Deviation
0
100
200
300
400
500
600
700
800
900
Reference mass, ng

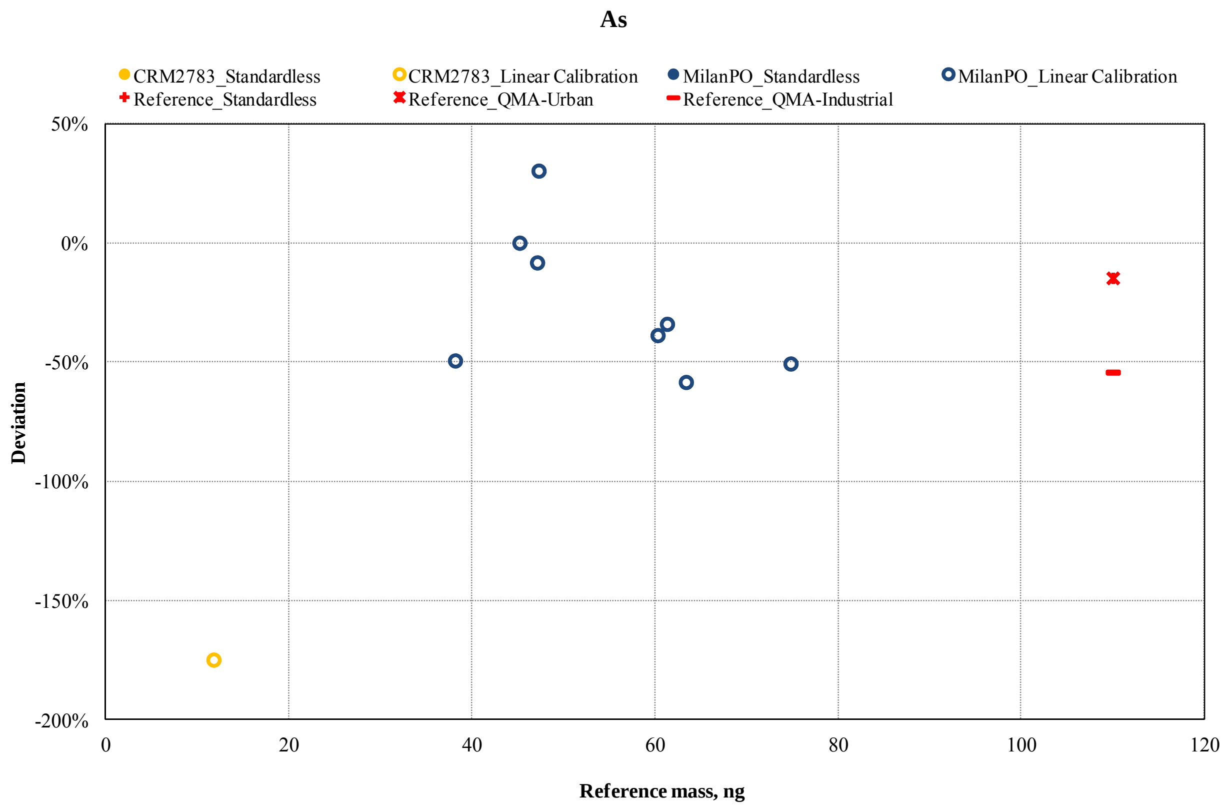

Cu
CRM2783_Standardless
CRM2783_Linear Calibration
MilanPO_Standardless
MilanPO_Linear Calibration
Reference_Standardless
Reference_QMA-Urban
Reference_QMA-Industrial
30%
20%
10%
0%
-10%
-20%
-30%
Deviation
0
1000
2000
3000
4000
5000
6000
Reference mass, ng

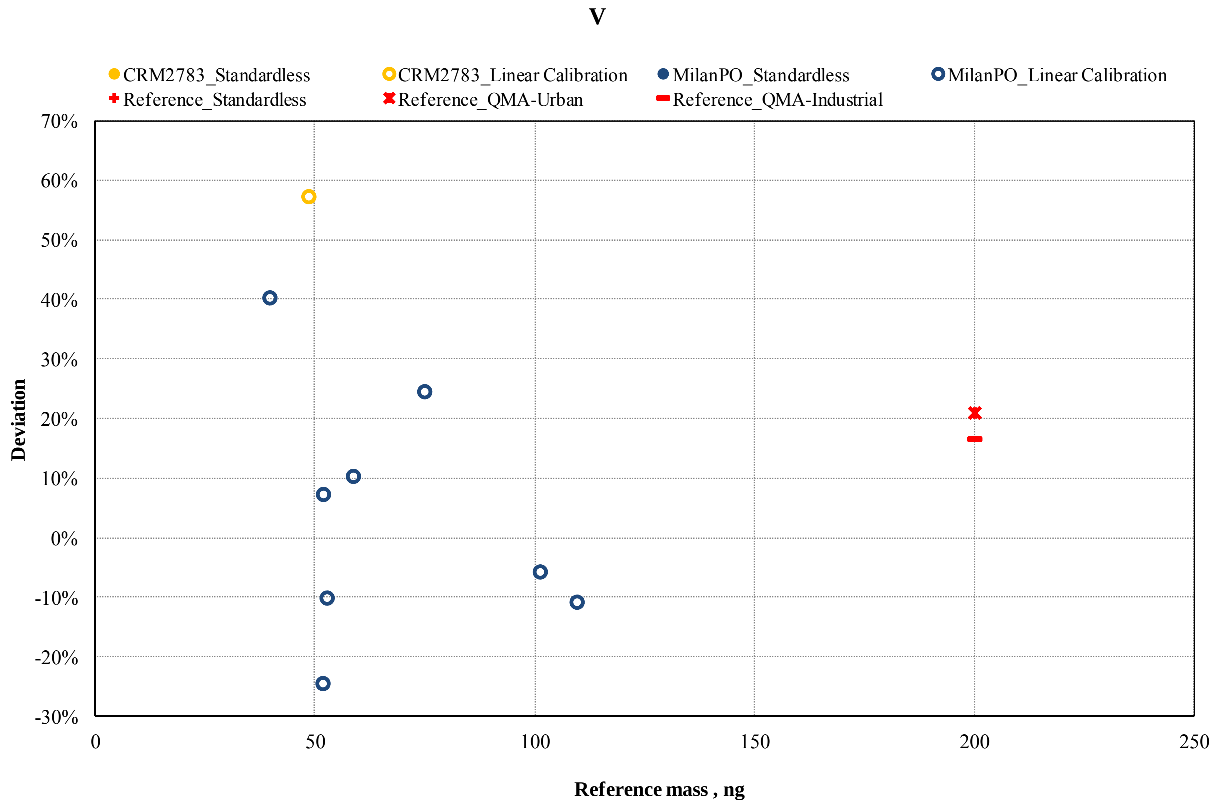

Mn
● CRM2783_Standardless
○ CRM2783_Linear Calibration
● MilanPO_Standardless
○ MilanPO_Linear Calibration
+ Reference_Standardless
✖ Reference_QMA-Urban
− Reference_QMA-Industrial
Deviation
40%
30%
20%
10%
0%
-10%
-20%
-30%
200
400
600
800
1000
1200
1400
1600
1800
2000
Reference mass, ng


Mo
● CRM2783_Standardless
○ CRM2783_Linear Calibration
● MilanPO_Standardless
○ MilanPO_Linear Calibration
+ Reference_Standardless
✖ Reference_QMA-Urban
− Reference_QMA-Industrial
Deviation
40%
30%
20%
10%
0%
-10%
-20%
-30%
-40%
100
150
200
250
300
350
400
450
500
550
600
Reference mass , ng


Ti
● CRM2783_Standardless
○ CRM2783_Linear Calibration
● MilanPO_Standardless
○ MilanPO_Linear Calibration
+ Reference_Standardless
✖ Reference_QMA-Urban
‒ Reference_QMA-Industrial
40%
30%
20%
10%
0%
-10%
-20%
-30%
-40%
Deviation
600
800
1000
1200
1400
1600
1800
2000
Reference mass , ng


Sr
● CRM2783_Standardless
○ CRM2783_Linear Calibration
● MilanPO_Standardless
○ MilanPO_Linear Calibration
+ Reference_Standardless
✖ Reference_QMA-Urban
‒ Reference_QMA-Industrial
15%
5%
-5%
-15%
-25%
-35%
Deviation
70
90
110
130
150
170
190
210
Reference mass , ng


As
● CRM2783_Standardless
○ CRM2783_Linear Calibration
● MilanPO_Standardless
○ MilanPO_Linear Calibration
+ Reference_Standardless
✖ Reference_QMA-Urban
▬ Reference_QMA-Industrial
50%
0%
-50%
-100%
-150%
-200%
Deviation
0
20
40
60
80
100
120
Reference mass, ng


V
● CRM2783_Standardless
○ CRM2783_Linear Calibration
● MilanPO_Standardless
○ MilanPO_Linear Calibration
+ Reference_Standardless
✖ Reference_QMA-Urban
▬ Reference_QMA-Industrial
70%
60%
50%
40%
30%
20%
10%
0%
-10%
-20%
-30%
Deviation
0
50
100
150
200
250
Reference mass , ng

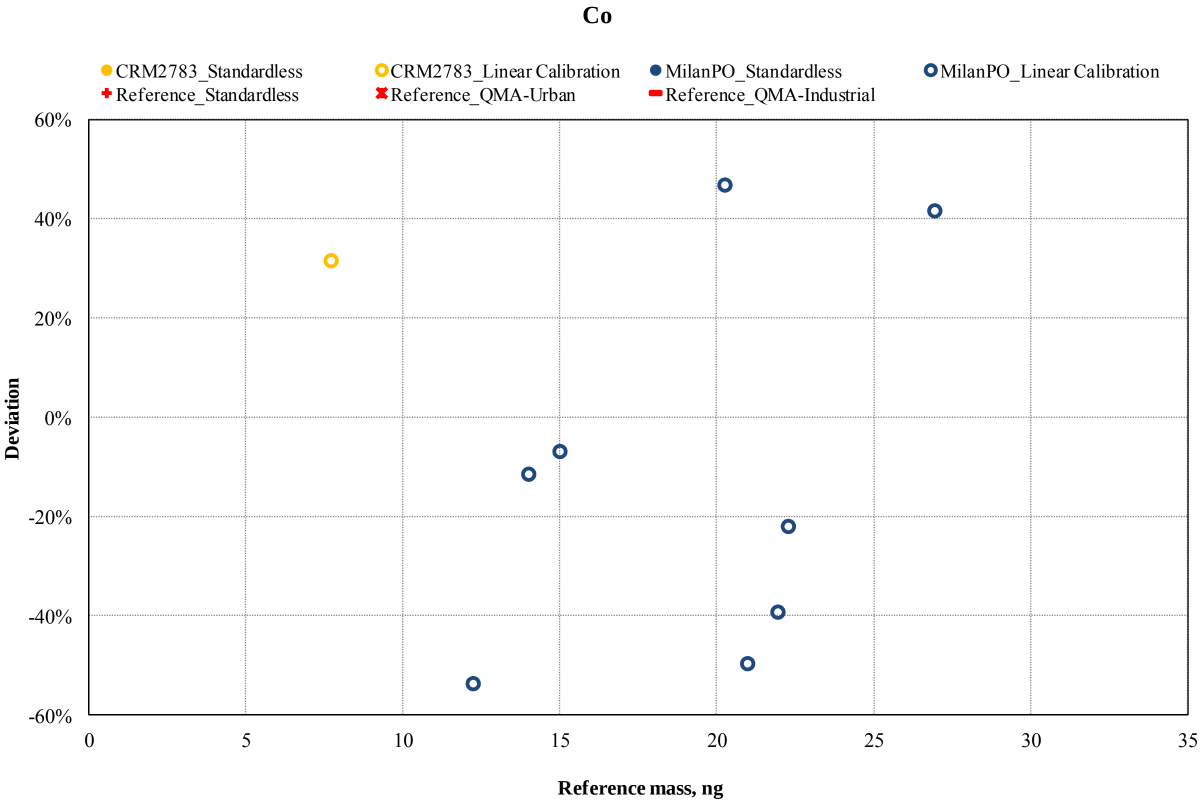


Figure 4: Relative deviations between EDXRF analysis and references values for a NIST CRM 2783, a few filters loaded at Milan PO (Teflon filter) and one Reference filter (an urban QMA filter). EDXRF analyses were quantified by Standardless method or Linear Calibration either with Teflon filters loaded at an urban site (Linear Calibration) or with QMA filters loaded at an urban site (QMA-Urban) or with QMA filters loaded at an industrial site (QMA-Industrial)

3.2 Evaluation of Method Detection Limit and Quantification Limit

The theoretical MDLs and LOQs (in ng) of 3 filter types by standardless EDXRF analysis are given in Table 3, where the elements are sorted by ascending atomic weight (Z). The MDLs for Teflon filter were generally lower than the quartz ones, most probably resulting from lower impurities in the Teflon filter and smoother surface (Robache et al., 2000[30]). The MDLs decreased with Z. This pattern was observed for all filter types. The concentrations of Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, Sr, Ti and Zn in the analyzed samples were found to be higher than LOQs with a few exceptions. Apart from these 14 elements, the concentrations of Si (in Teflon filters only), Cl, S and Br (for over 50% of samples) were found higher than those LOQs, meaning that EDXRF was sensitive enough to quantify them in the filters of this study.

EN 14902[10] sets the minimum MDLs as 3 times SD of laboratory blanks for Pb, Ni, Cd and As analyzed by ICP-MS or GFAAS to be lower than 10% of the limit values (LV) of EU Directives. The estimated mass of Pb, Ni, Cd and As on filter at LVs of ambient air correspond to 27500, 1100, 275 and 330 ng, respectively assuming 55 m^3 sampled per filter. It can be observed in Table 3 that the MDLs of Pb and Ni are considerably lower than 10% of the LV whereas the MDLs of Cd and As were higher than MDLs and still lower than LOQs.

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[30] Robache, A., Mathé, F., Galloo, J.C., Herbin, M., Malet, B., 2000. Conditions de Prélèvements des Particules en Vue de l'analyse des Métaux. Ecole des mines de Douai, Département Chimie et Environnement. http://www.lcsqa.org/system/files/Etude3_0.pdf.

Table 3: Method detection limits MDLs and quantification limits (in ng on each filter) of various filter types

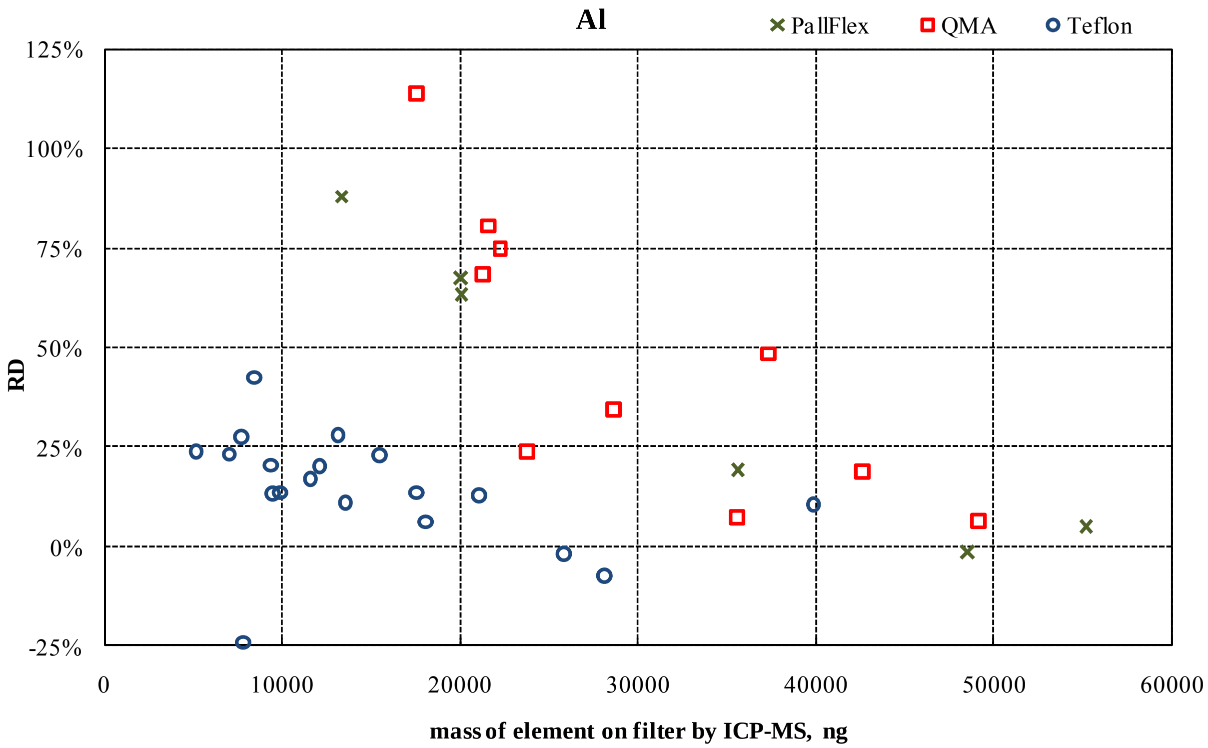
Element	Teflon		QMA		PallFlex	
	MDL	LOQ	MDL	LOQ	MDL	LOQ
Mg	79	264	1151	3836	924	3081
Al	7	24	1318	4395	1298	4326
Si	893	2976	268001	893338	11607	38691
S	59	198	419	1396	192	639
Cl	47	156	303	1011	127	423
K	119	396	126	420	135	451
Ca	503	1676	410	1367	335	1118
Ti	41	136	84	280	19	63
V	39	131	59	198	55	184
Cr	19	62	123	411	48	160
Mn	30	98	46	153	18	59
Fe	182	607	1529	5095	875	2917
Co	51	169	41	136	89	297
Ni	5	16	20	66	6	22
Cu	83	277	42	142	117	389
Zn	49	163	115	383	450	1501
As	149	495	105	351	172	572
Br	27	91	17	56	23	75
Sr	22	74	27	91	64	212
Mo	68	228	174	581	111	369
Cd	220	733	152	507	439	1462
Sn	328	1093	153	509	274	912
Sb	464	1546	462	1541	499	1662
Pb	82	273	41	137	41	138

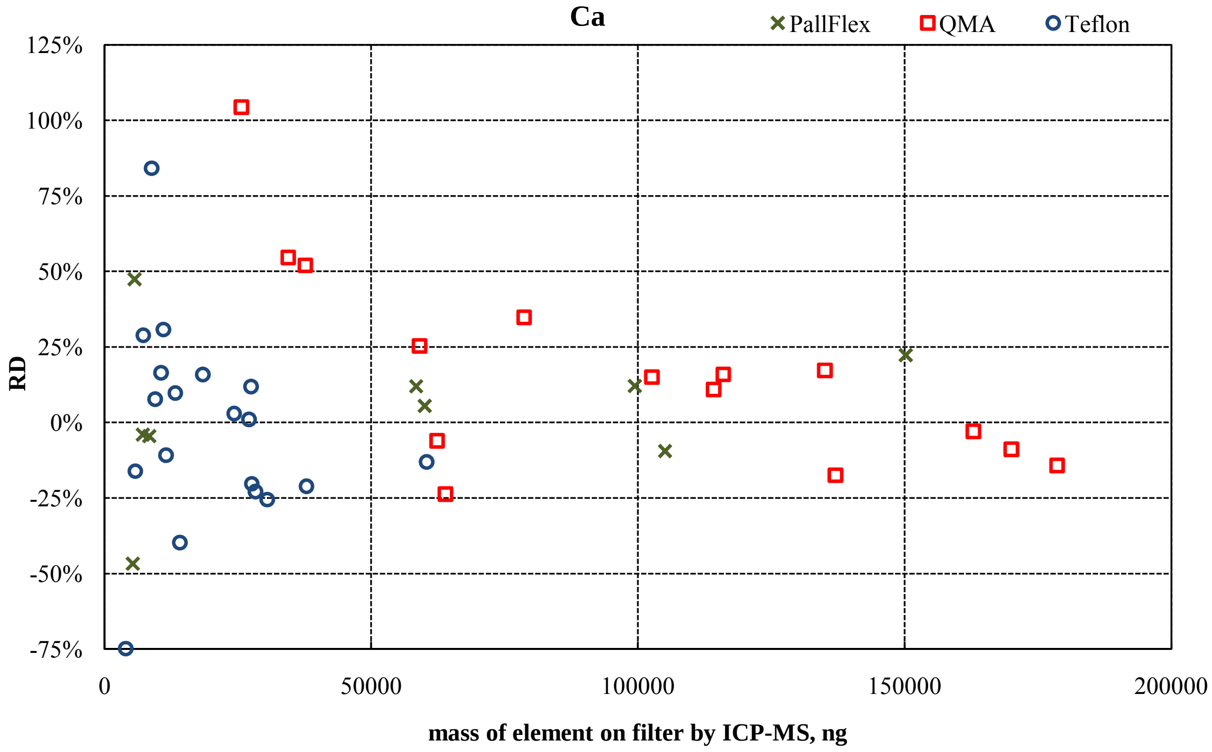
3.3 Evaluation of the Results of Standardless EDXRF Analysis and ICP-MS

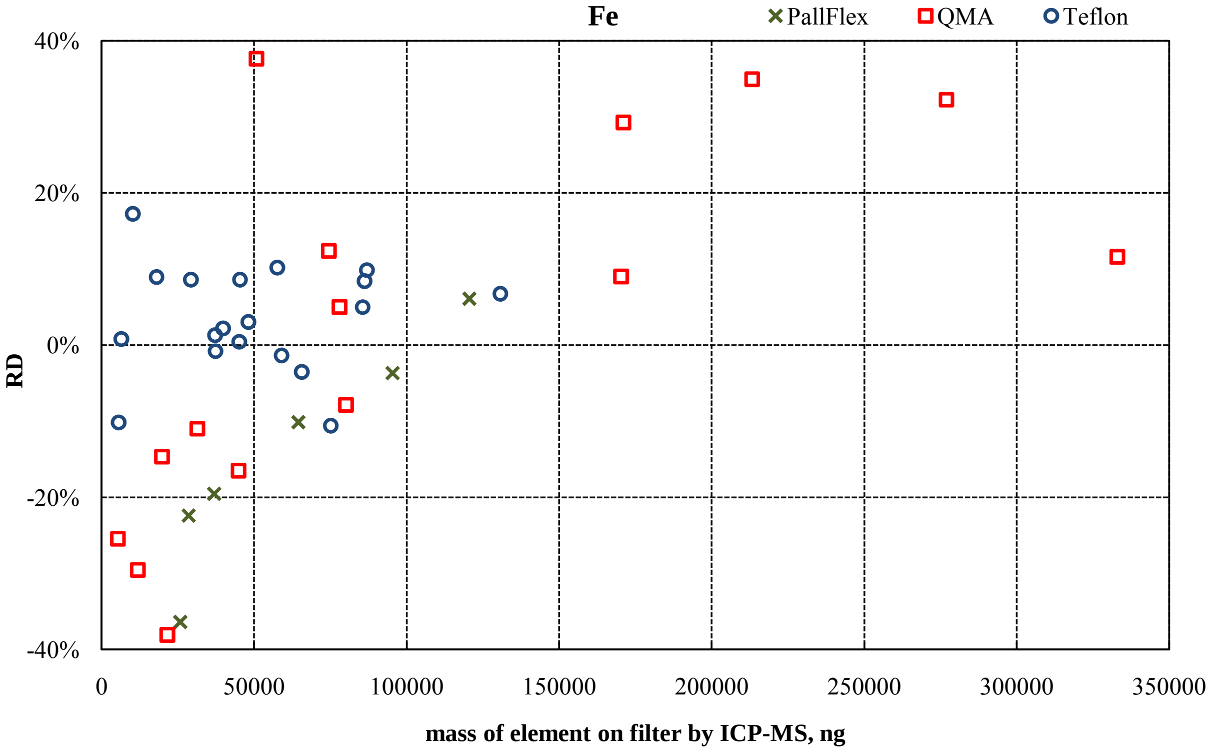
The variations of RD per element versus elemental masses determined by ICP-MS are plotted in Figure 5. Al, Ca, K, Zn, Pb, Mn, Cu and Ti exhibited similar pattern with RD values decreasing towards to 0 with elemental concentrations for all types of filters. This might be attributed to the insufficient sensitivity of EDXRF to quantify these elements at low concentrations. At very low Al concentrations (<4000 ng), the deviations associated with quartz filters increased sharply up to 700% (Not shown in Figure 5). Fe showed constant deviations between -10% and 10% for Teflon, a strong relationship between deviations and mass for PallFlex and huge random variation for QMA. Mg, Ni and Sr showed elemental mass independent deviations.

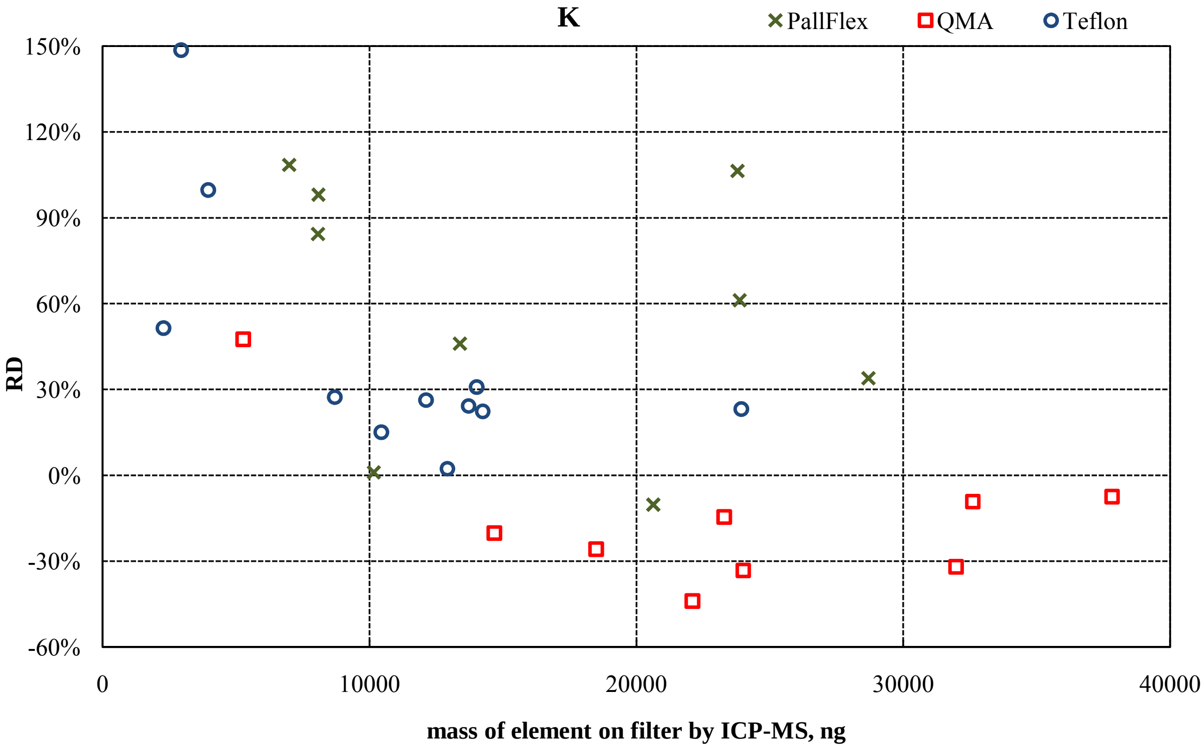
For QMA filters, the RD values of Ni showed two different patterns. At the industrial site, very high negative RD values (about -75 %) were computed particularly for masses higher than 1000 ng. At the urban sites, the RD values ranged between -5 and 75 % for masses between 350 and 600 ng. The two different patterns suggested that, for QMA filters, the standardless EDXRF analysis might depends on the type of sampling site. The deviations of Cr-Teflon and Mo-Teflon were mass independent whereas they remained constant at -40% of Cr and -25% of Mo for PallFlex and QMA.

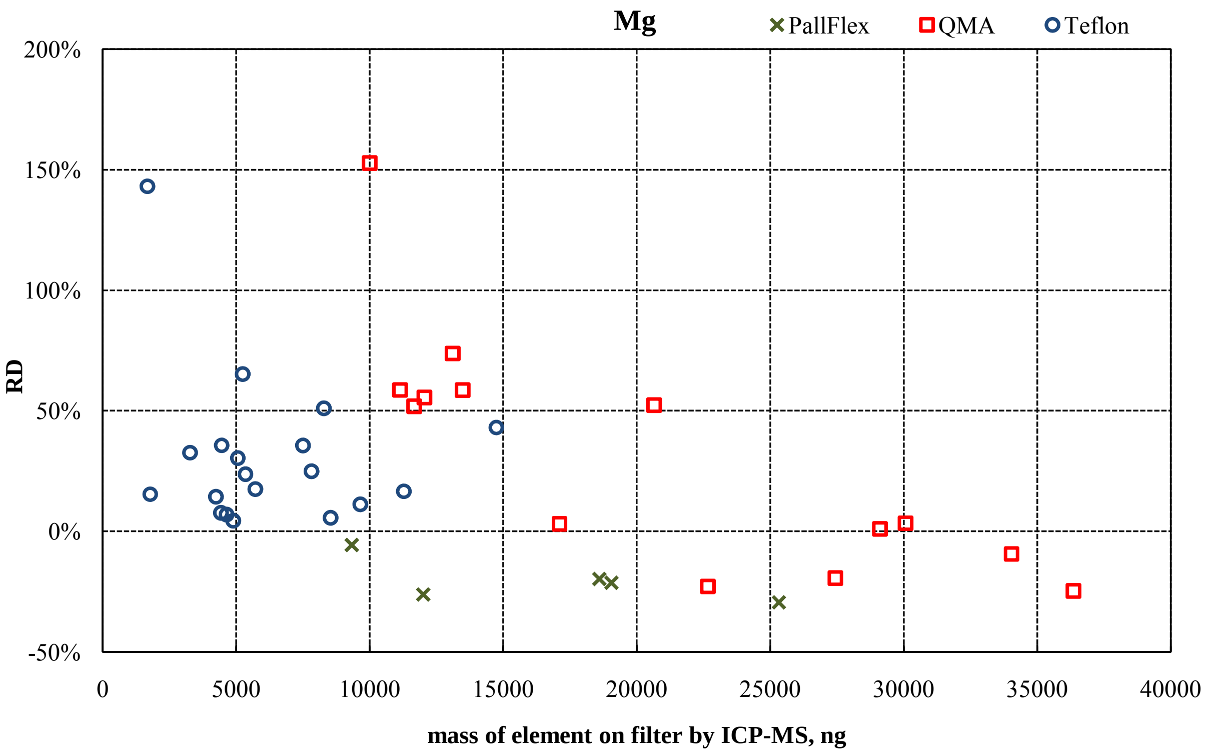
Figure 6 shows that the RAD_m values were lower than 25% for most of elements. The elements showing very high RD values at low elemental concentrations such as Al, Ti, K, Zn, and Pb for both types of quartz filters have higher RAD_m values. Ni exhibited high RAD_m values for each type of filters. The RAD_m of Cr of both quartz filters remained around 40%, resulting from the constant RD values. The elemental concentrations close to MDLs increased the RAD_m values. The elements with low S/B such as Al, Ca, K and Ti for quartz filters have high random variability. In most of the case, the deviations of Teflon filters are lower than the quartz ones. This might be attributed the lower impurity and smoother filter surface of Teflon filters.

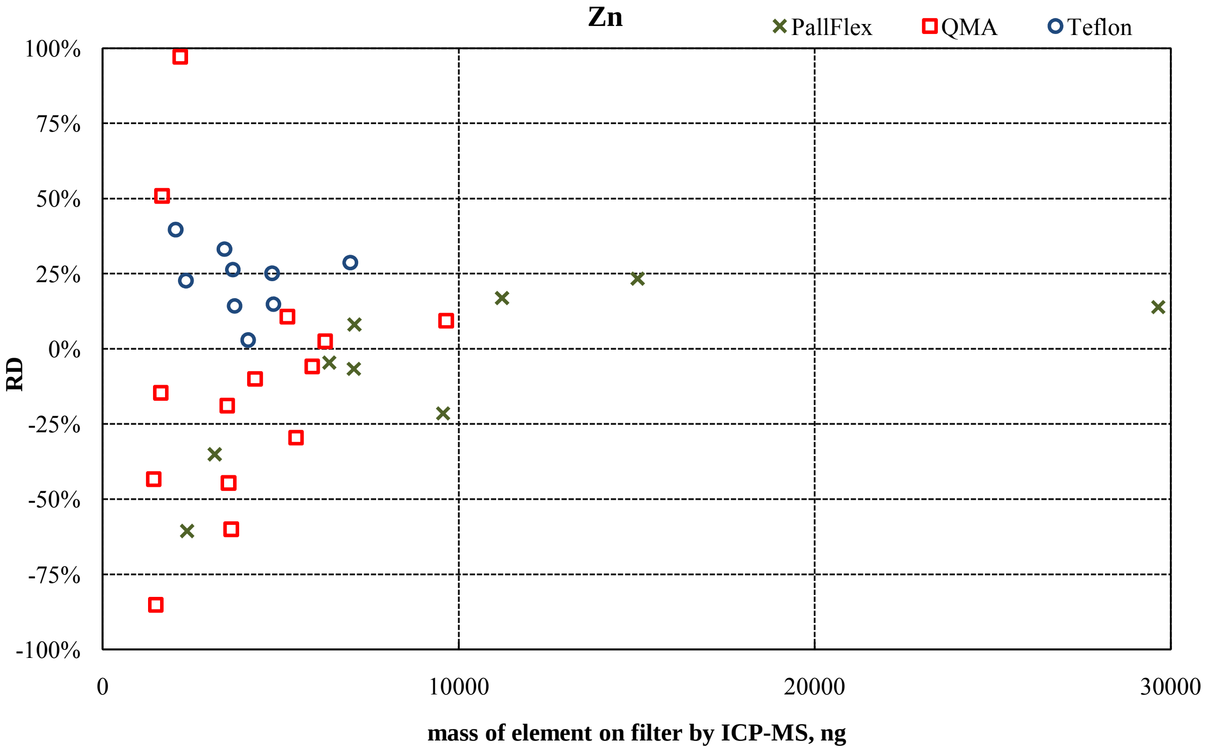

Al
× PallFlex
□ QMA
○ Teflon
125%
100%
75%
50%
25%
0%
-25%
RD
0
10000
20000
30000
40000
50000
60000
mass of element on filter by ICP-MS, ng

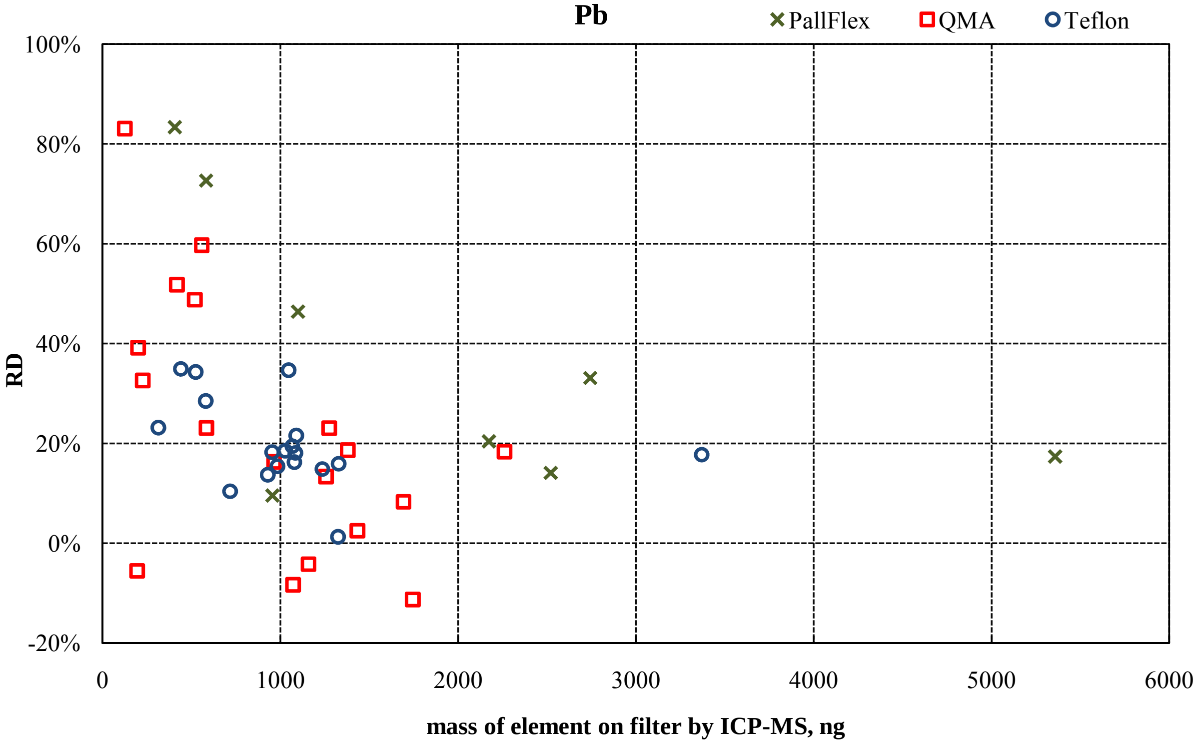

Ca
× PallFlex
□ QMA
○ Teflon
125%
100%
75%
50%
25%
0%
-25%
-50%
-75%
RD
0
50000
100000
150000
200000
mass of element on filter by ICP-MS, ng

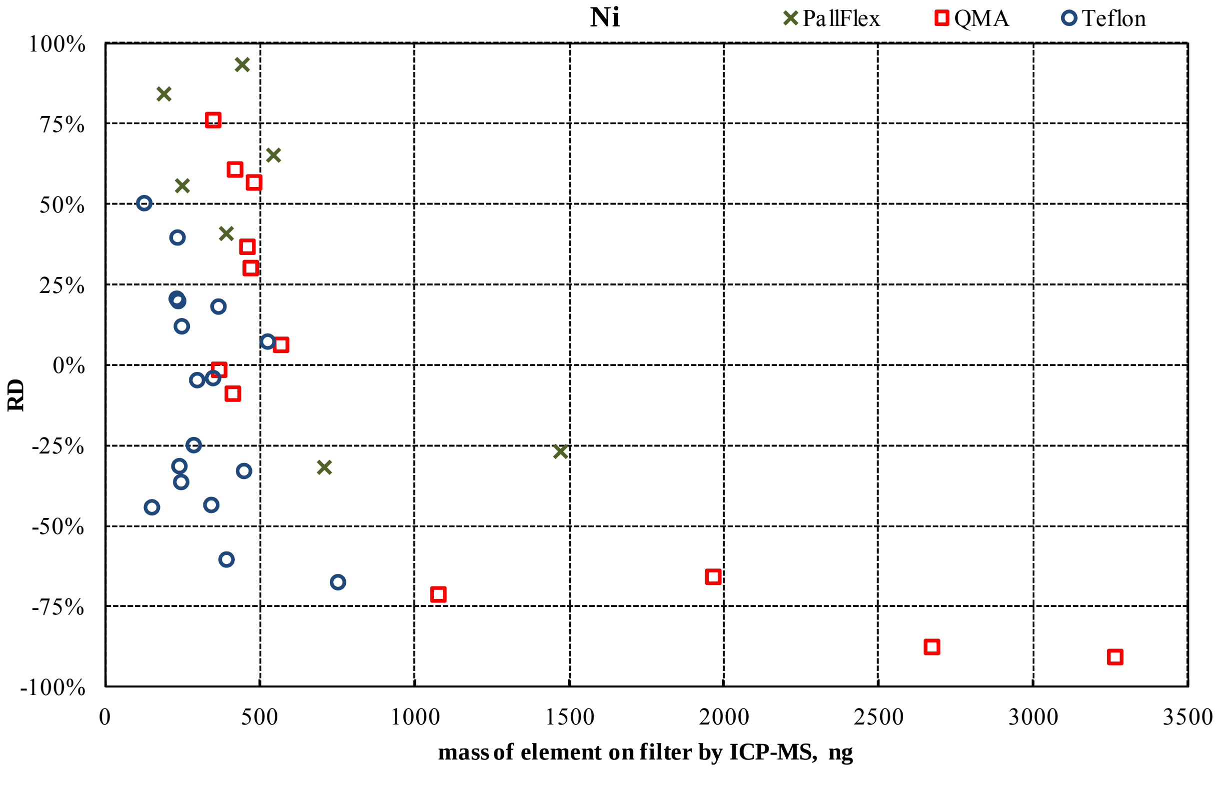

Fe
× PallFlex
□ QMA
○ Teflon
40%
20%
0%
-20%
-40%
RD
0
50000
100000
150000
200000
250000
300000
350000
mass of element on filter by ICP-MS, ng

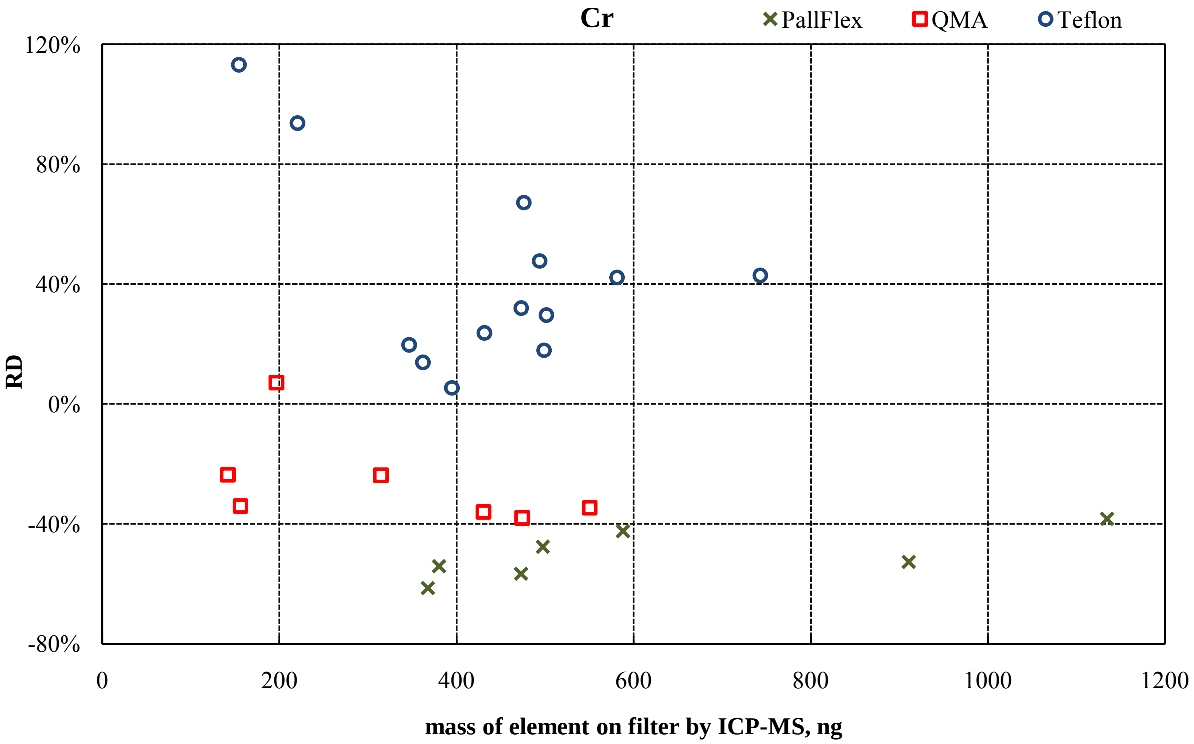

K
× PallFlex
□ QMA
○ Teflon
150%
120%
90%
60%
30%
0%
-30%
-60%
RD
0
10000
20000
30000
40000
mass of element on filter by ICP-MS, ng

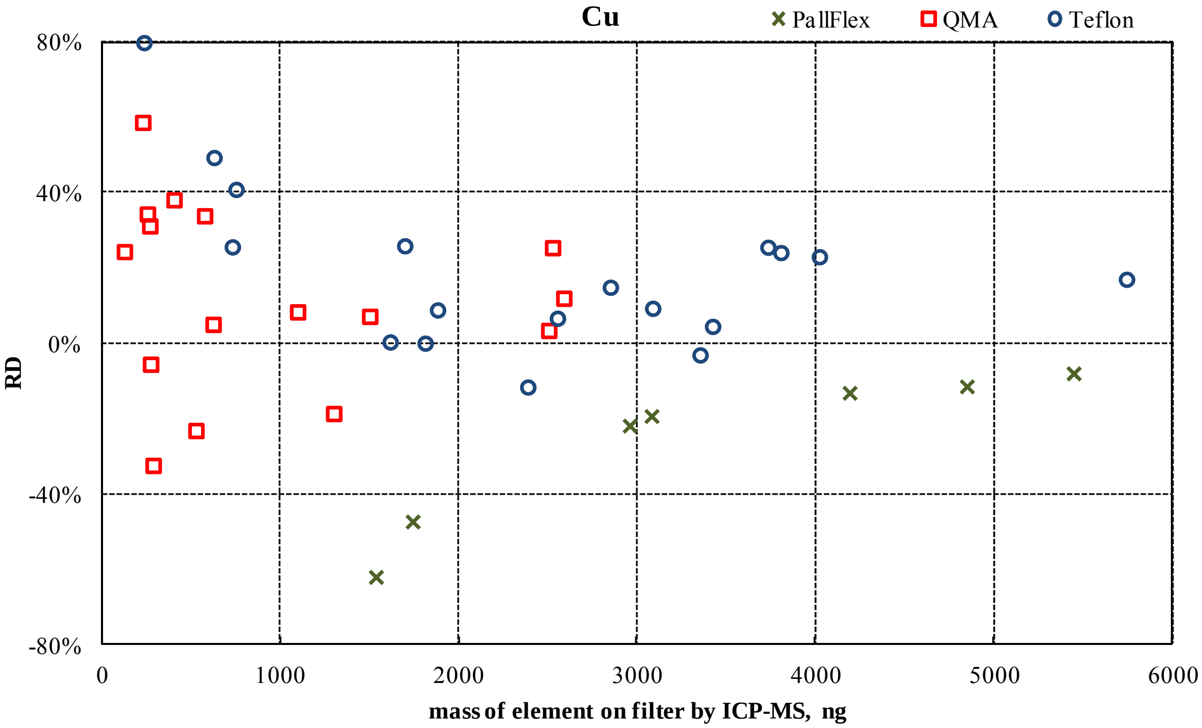

Mg
× PallFlex
□ QMA
○ Teflon
RD
200%
150%
100%
50%
0%
-50%
0
5000
10000
15000
20000
25000
30000
35000
40000
mass of element on filter by ICP-MS, ng

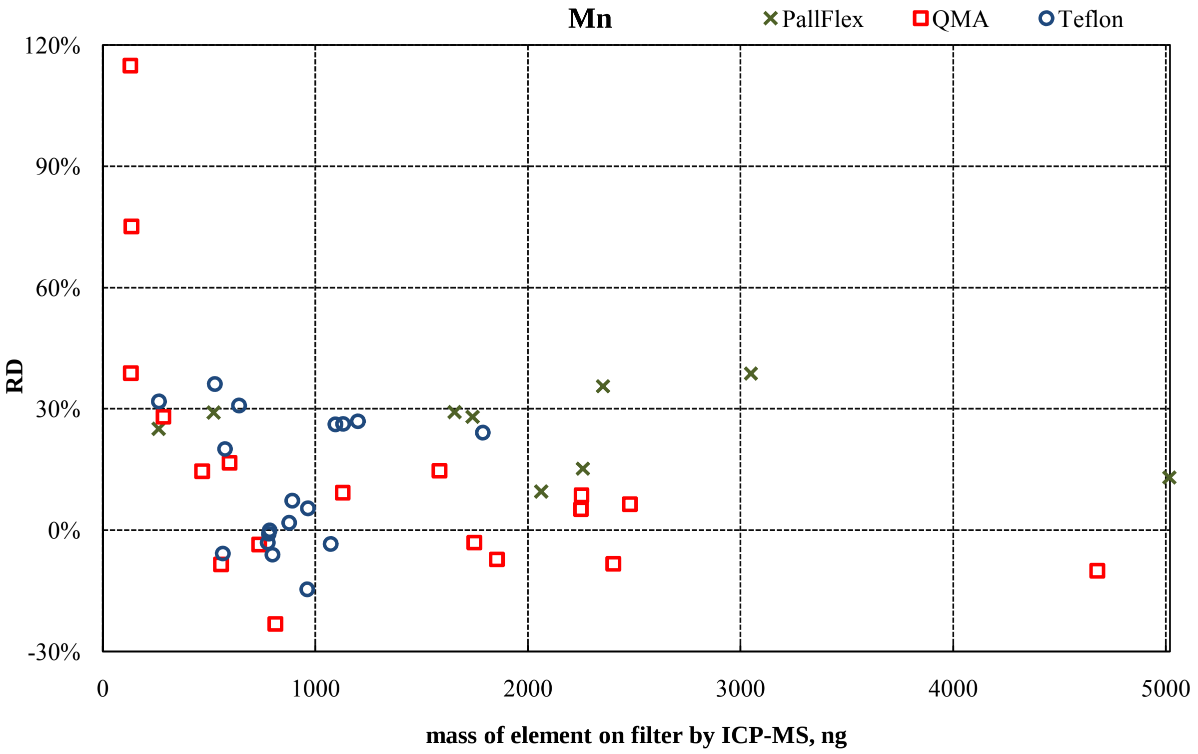

Zn
× PallFlex
□ QMA
○ Teflon
RD
100%
75%
50%
25%
0%
-25%
-50%
-75%
-100%
0
10000
20000
30000
mass of element on filter by ICP-MS, ng


Pb
× PallFlex
□ QMA
○ Teflon
100%
80%
60%
40%
20%
0%
-20%
RD
0
1000
2000
3000
4000
5000
6000
mass of element on filter by ICP-MS, ng

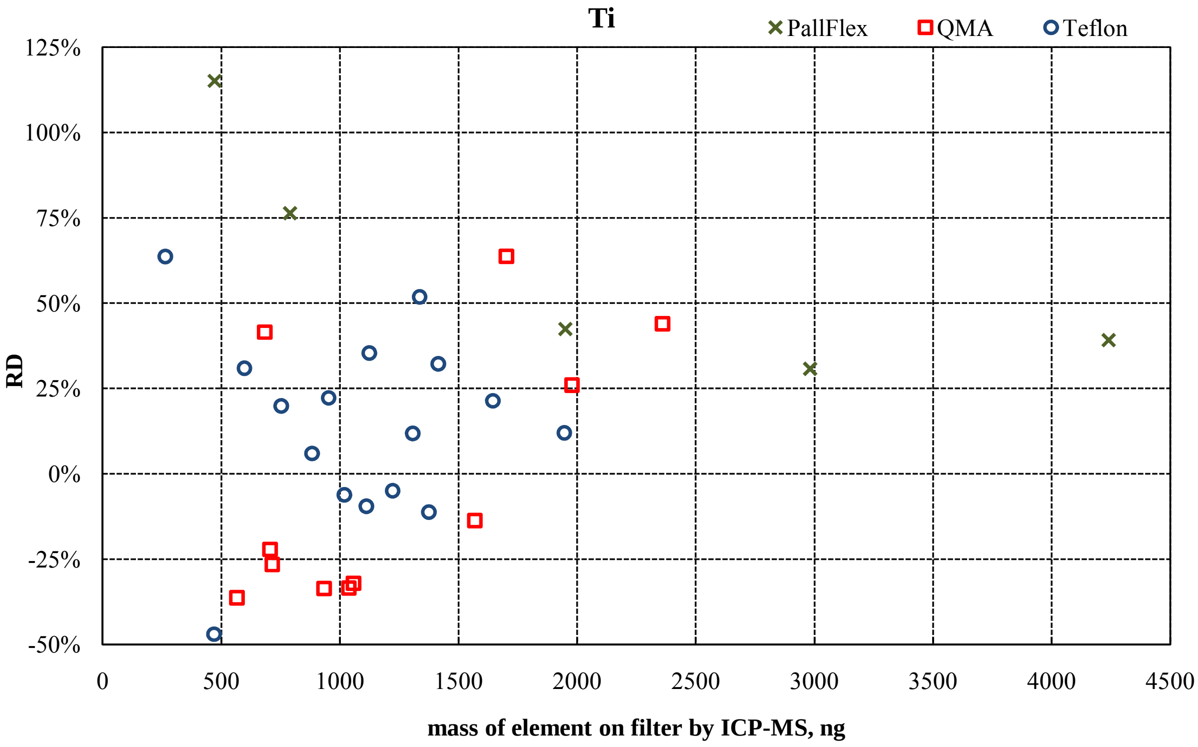

Ni
× PallFlex
□ QMA
○ Teflon
100%
75%
50%
25%
0%
-25%
-50%
-75%
-100%
RD
0
500
1000
1500
2000
2500
3000
3500
mass of element on filter by ICP-MS, ng


Cr
× PallFlex
QMA
Teflon
120%
80%
40%
0%
-40%
-80%
RD
0
200
400
600
800
1000
1200
mass of element on filter by ICP-MS, ng


Cu
× PallFlex
QMA
Teflon
80%
40%
0%
-40%
-80%
RD
0
1000
2000
3000
4000
5000
6000
mass of element on filter by ICP-MS, ng


Mn
PallFlex
QMA
Teflon
120%
90%
60%
30%
0%
-30%
RD
0
1000
2000
3000
4000
5000
mass of element on filter by ICP-MS, ng

c


Ti
PallFlex
QMA
Teflon
125%
100%
75%
50%
25%
0%
-25%
-50%
RD
0
500
1000
1500
2000
2500
3000
3500
4000
4500
mass of element on filter by ICP-MS, ng

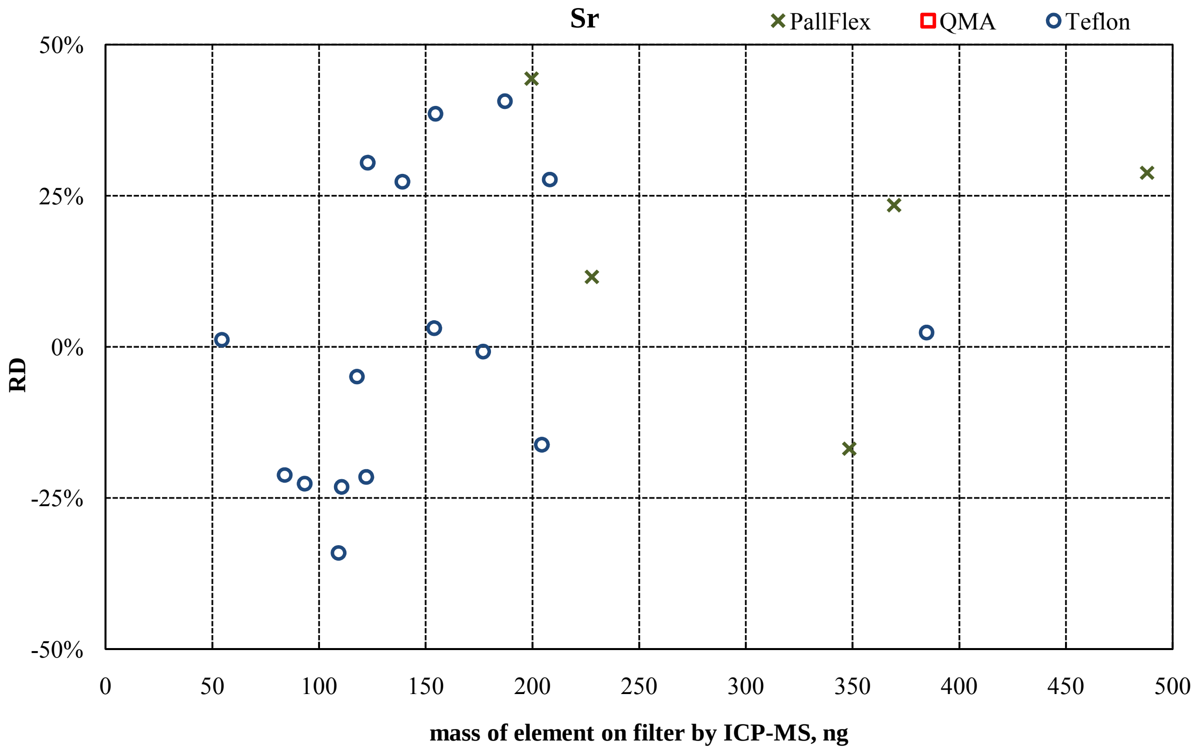


Figure 5: Relative deviation (RD, %) of EDXRF versus elemental masses measured by ICP-MS. For Al, 3 PallFlex samples (3140 ng-718%, 4050 ng-531%, 3995 ng-485%) and 1 QMA sample (5071 ng-594%), for Pb, 2 PallFlex samples (170 ng-204%, 5358 ng-17%), for Ni, 1 PallFlex sample (108 ng-434%), for Mn, 1 PallFlex sample (5017 ng, 13%) and 1 QMA sample (4678 ng, -10%), forTi, 2 PallFlex sample (191 ng-276%, 128 ng-506%) and for Zn, 1 PallFlex sample (29648 ng-14%) are out of scale for better wiev

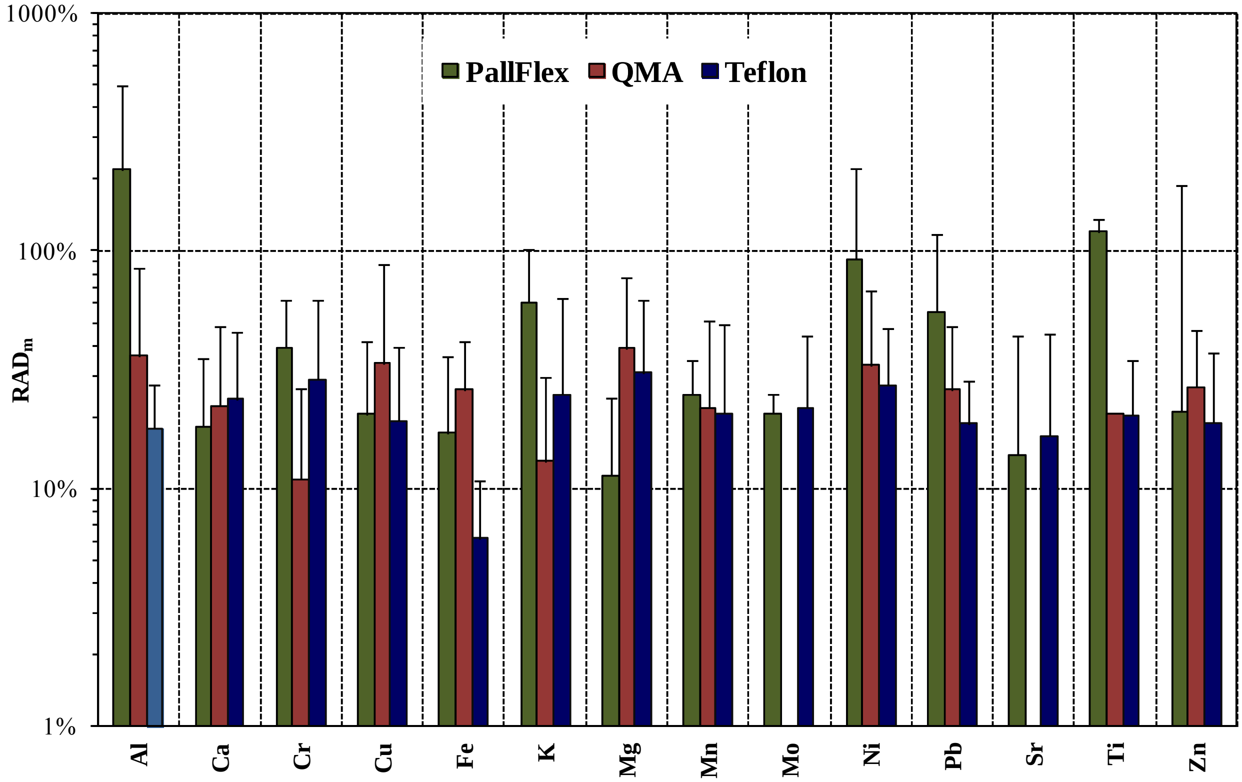


Figure 6: The mean relative absolute deviation (RAD_m, %) and standard deviation (Error bars) between EDXRF and ICP-MS per filter type

3.4 Evaluation and Comparison of Measurement Uncertainty of Standardless Analysis

3.4.1 *Laboratory Uncertainty (U_{GUM})*

The magnitude of the contributions of all factors to the relative expanded uncertainties, $U_{r,GUM}$, are given in Figure 7 considering the average of all filters for each type of filters. I_{net} was identified as one of the major contributors for some elements, with higher contributions at low concentrations. The variations of the contribution of I_{net} for each element are given in Figure 8. Generally, the contribution of I_0 was higher than I. At very low concentrations, the contribution of I_{net} increased because of worsened repeatability of I. The contribution of K_i was higher than 12%. The contributions of A, A_d and m_{PM} were found to be about 15, 3 and 9%, respectively. However, the contribution of these parameters to the total measurement uncertainty decreased because of the correlations between A and m_{PM} (-8%) and between A_d and m_{PM} (-5%). The mass absorption coefficient, μ_i, had no significant effect on $U_{r,GUM}$, except for Al and Mg, which was influenced by the type of selected Rest configurations. In the same way, contributions to the total measurement uncertainties lower than 1% were estimated for the interference.

For Teflon filters, $U_{r,GUM}$ was estimated between 25-35% except for Mo (46%). $U_{r,GUM}$ was found to be independent of elemental masses except for Mo and Ti, whose $U_{r,GUM}$ increased at low concentrations resulting from higher I_{net} contributions. For PallFlex, $U_{r,GUM}$ was estimated between 27-35% except for Ni (46%), Cu (48%), Mg (49%) and Sr (70%). High values of $U_{r,GUM}$ for Cu and Ni resulted from an increase of the I_{net} contribution at low elemental masses. I_{net} contributions to $U_{r,GUM}$ for Mg (9%) and Sr (23%) were higher than the other elements (1-2%).

For QMA, $U_{r,GUM}$ for Al, Br, Cu, Mg, Mn, Pb and S were estimated between 25 and 35% apart for Cr (55%) and Sr (39%) resulting from high I_{net} contributions. At low elemental masses, higher I_{net} contributions yielded an increase of $U_{r,GUM}$ for Ca, Fe, K, Ni, Ti and Zn up to 51, 100, 43, 46, 50 and 91%, respectively. Although the EDXRF fluorescence intensities and the ICP-MS results for As and V were highly correlated, the standardless EDXRF analysis could not succeed in quantifying the studied samples.

For each element and type of filter, orthogonal regression of EDXRF values versus ICP-MS ones was used to compare both techniques and to estimate the uncertainty of EDXRF results ($U_{r,DIR}$) using Equation 8. The regression slope and intercepts with their standard uncertainties are given in Table 4. It should be noted that due to the large noise of the results, the orthogonal regression of Ni for QMA filters gave a negative slope, and huge intercept. Therefore, Ni for QMA filters was discarded for the orthogonal regression and $U_{r,DIR}$ calculation. This table shows that the scattering of the slopes and intercepts of all elements is higher for quartz filters than for Teflon. The number of elements determined on QMA was lower. The mean slope of the regression lines was close to 1 with better homogeneity for Teflon filters (1.17 ± 0.17 (1s)) compared to PallFlex (1.06 ± 0.34) and QMA (0.96±0.44). Similarly, better homogeneities of the intercept of the regression lines were observed for the Teflon filters (-2.2 % ± 14 % (1SD)) compared to PallFlex (1% ± 43 % m/m) and QMA (18% ± 58 %). This latter figure indicates high differences between the blank values of ICP-MS and EDXRF for QMA filters likely caused by the addition of borosilicate glass. The slopes higher than 1 suggest an insufficient digestion of PM on the filters creating a negative bias for the ICP-MS results.

Table 4: Slope and intercept of the orthogonal regression lines of EDXRF versus ICP-MS masses in ng for 3 types of filters. b_1 represents the slope ± standard uncertainty whilst b_0 is the intercept (divided by arithmetic mean of ICP-MS, $\overline{x}$) ± standard uncertainty divided by the intercept. (n.a.: Not available due to lack of the orthogonal regression)

Element	Teflon		PallFlex		QMA	
		b_1		b_1		b_1
	n	b_0 (100*b_0/$\overline{x}$)	n	b_0 (100*b_0/$\overline{x}$)	n	b_0 (100*b_0/$\overline{x}$)
Al	19	1.03±0.05	9	0.61±0.05	11	0.76±0.17
		9±61		93±7		83±22
Ca	19	0.84±0.06	9	1.16±0.07	15	0.85±0.06
		10±75		-7±136		28±25
Cr	13	1.45±0.18	7	0.66±0.07	7	0.57±0.08
		-8±248		-14±49		14±61
Cu	18	1.17±0.05	7	1.11±0.02	17	1.12±0.05
		-4±172		-35±7		-2±433
Fe	19	1.06±0.03	7	1.13±0.03	18	1.26±0.04
		-2±134		-25±16		-11±57
K	11	1.11±0.08	9	1.80±0.33	9	0.88±0.14
		17±53		-27±137		-9±177
Mg	19	1.37±0.09	5	0.64±0.08	16	0.15±0.12
		-9±117		23±57		83±16
Mn	19	1.25±0.09	9	1.18±0.08	18	0.93±0.03
		13±76		5±171		8±53
Mo	17	1.21±0.07	9	1.04±0.15	-	-
		-0.4±1677		-24±63		
Ni	16	1.20±0.23	8	0.56±0.17	n.a.	n.a
		-32±81		75±29		n.a.
Pb	19	1.12±0.05	9	1.13±0.04	18	1.05±0.06
		6±89		14±39		8±91
Sr	16	1.24±0.12	5	1.41±0.36	-	-
		-21±73		-37±160		
Ti	16	1.33±0.14	7	1.24±0.04	11	1.84±0.20
		-19±80		22±20		-75±30
Zn	9	1.27±0.11	9	1.23±0.06	14	1.19±0.14
		-5±230		-18±40		-25±64

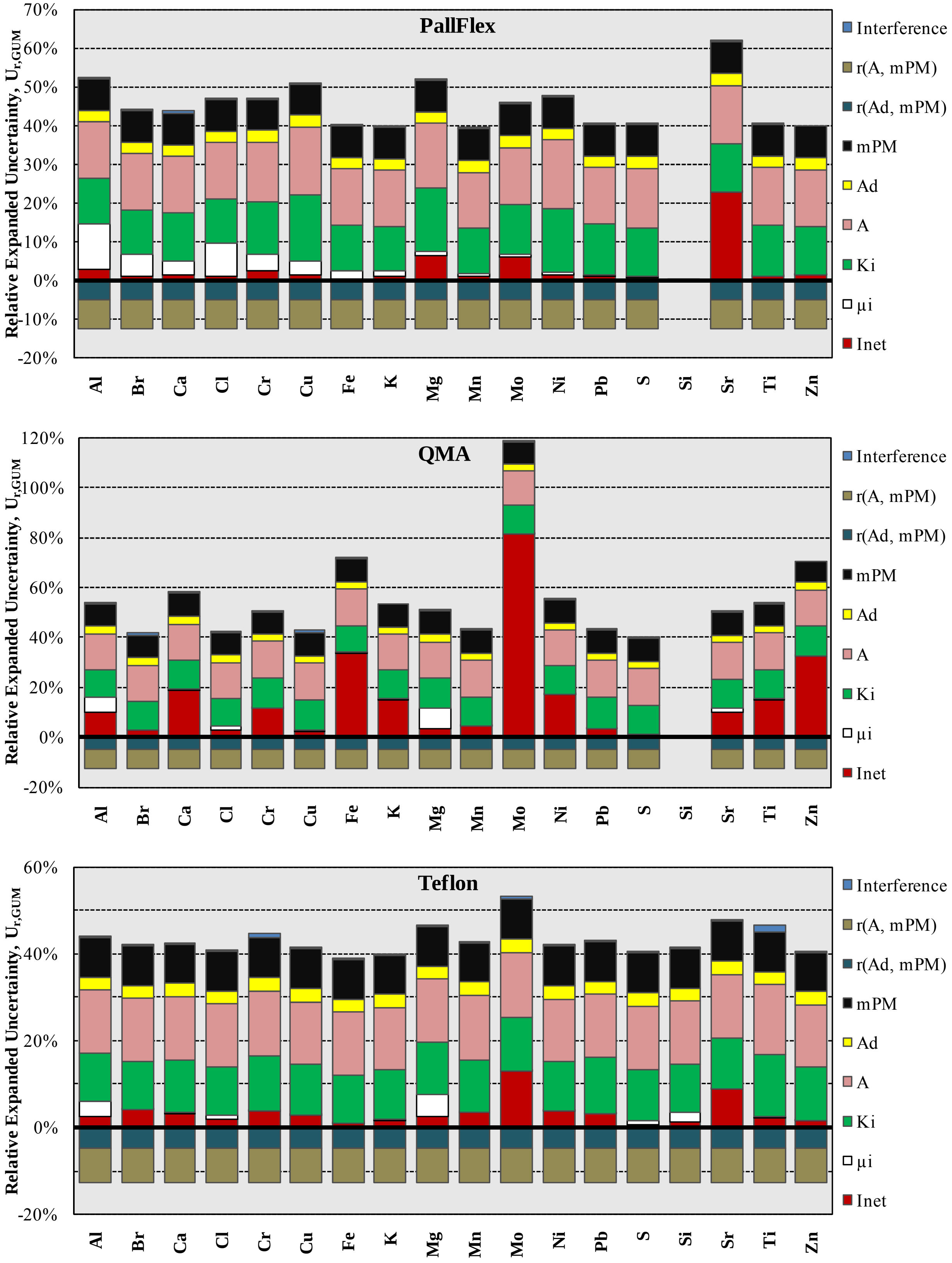
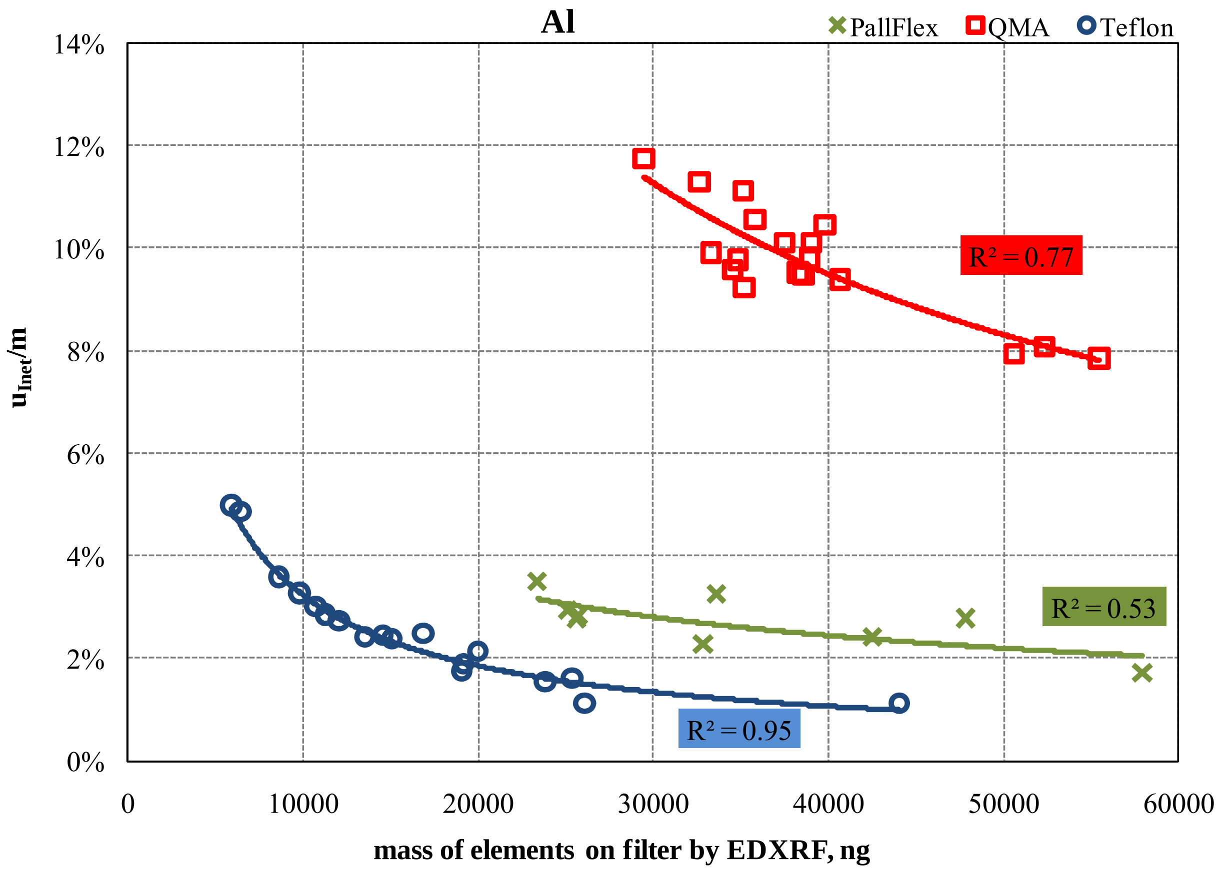
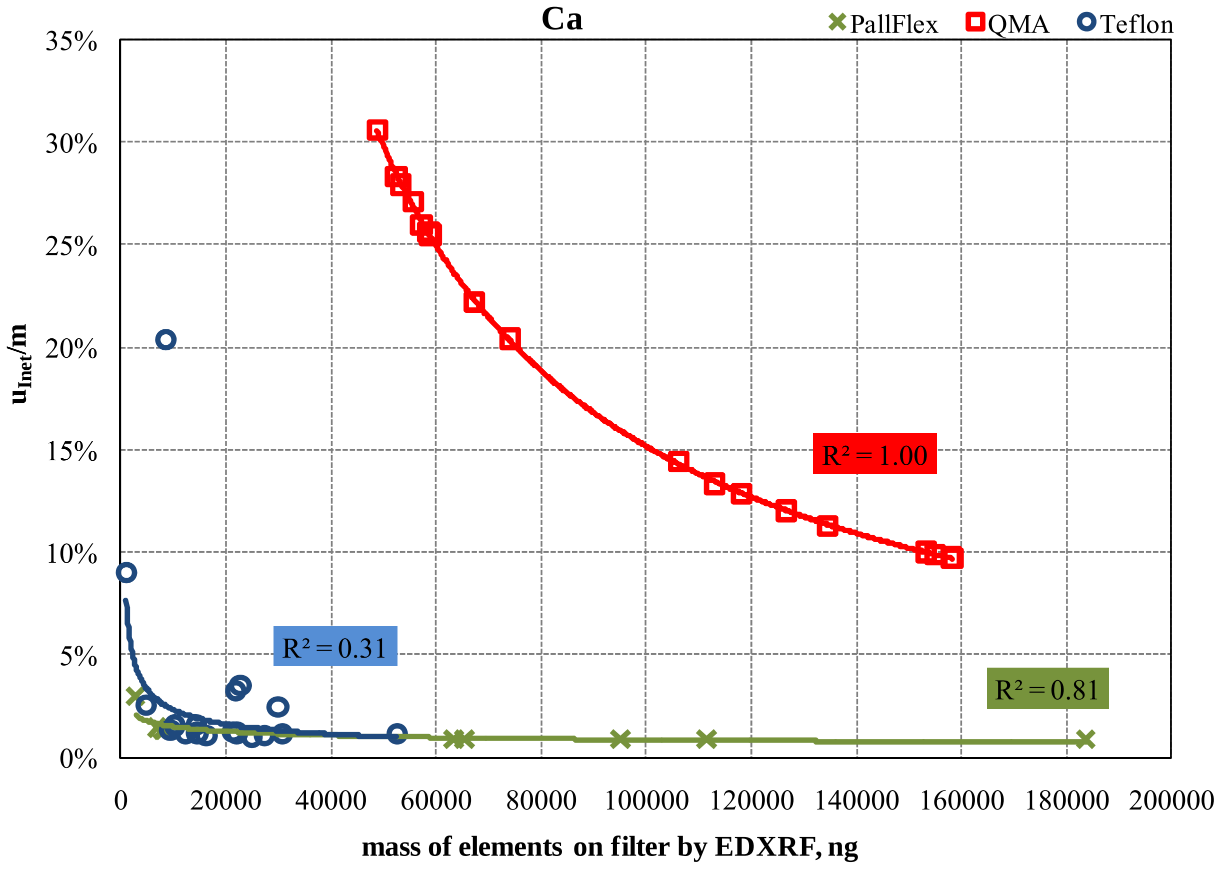
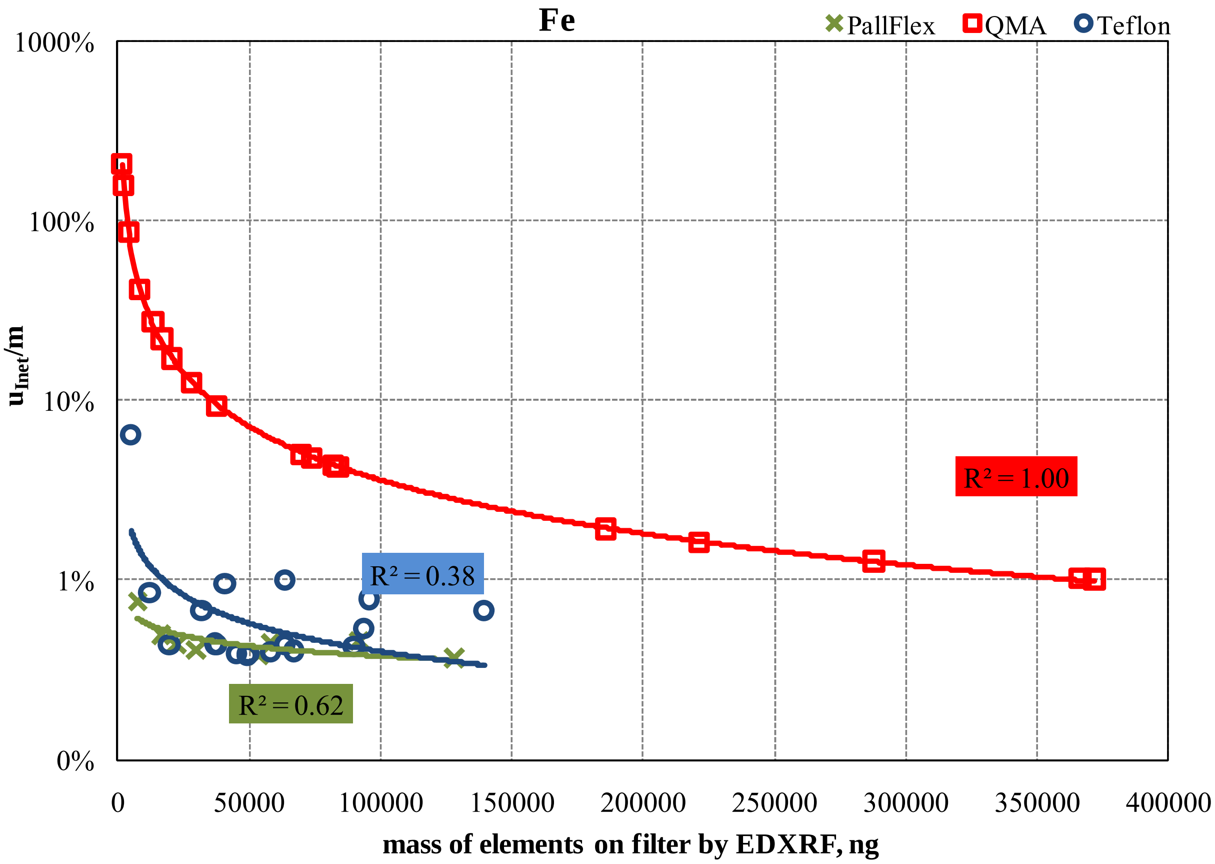
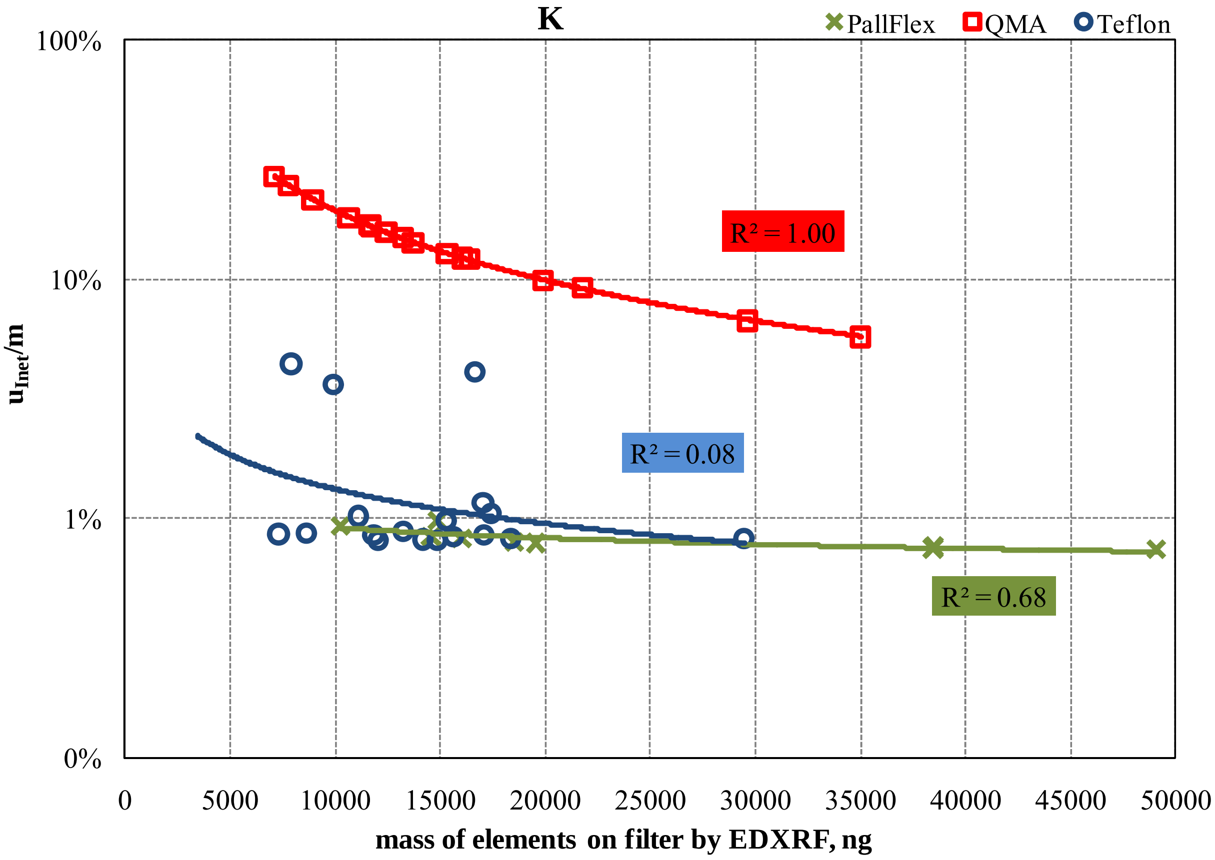


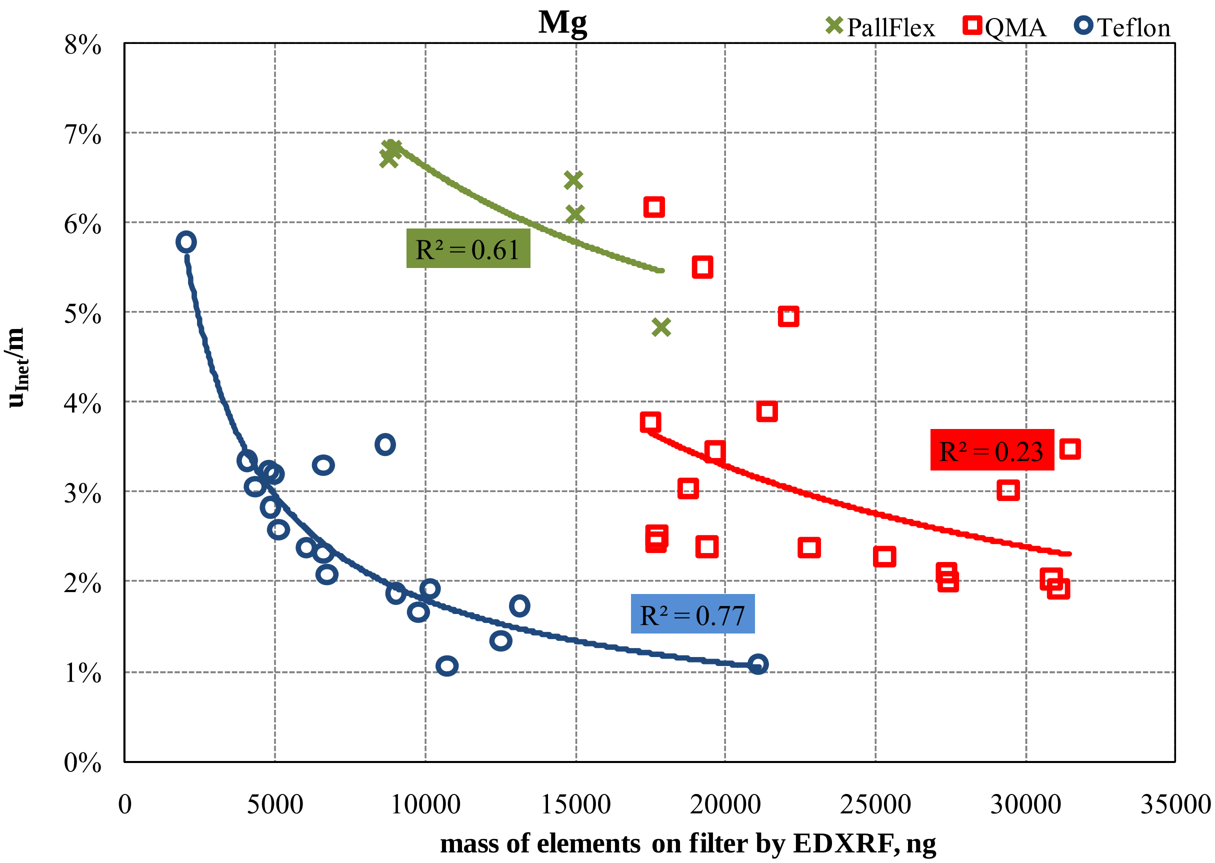
Figure 7: Average contributions of parameters to $U_{r,GUM}$ for 3 types of filter. I_{net} refers $I-I_0$. r denotes the contributions of the correlations between correlated variables, A is the excited area; A_d is the PM deposited area, m_{PM} is the mass of PM_{10}; K_i is the ratio of counts to mass of element i determined by initial calibration; μ_i is the mass absorption coefficient of element i


Al
PallFlex
QMA
Teflon
14%
12%
10%
8%
6%
4%
2%
0%
u_{Inet}/m
0
10000
20000
30000
40000
50000
60000
mass of elements on filter by EDXRF, ng
R² = 0.77
R² = 0.53
R² = 0.95

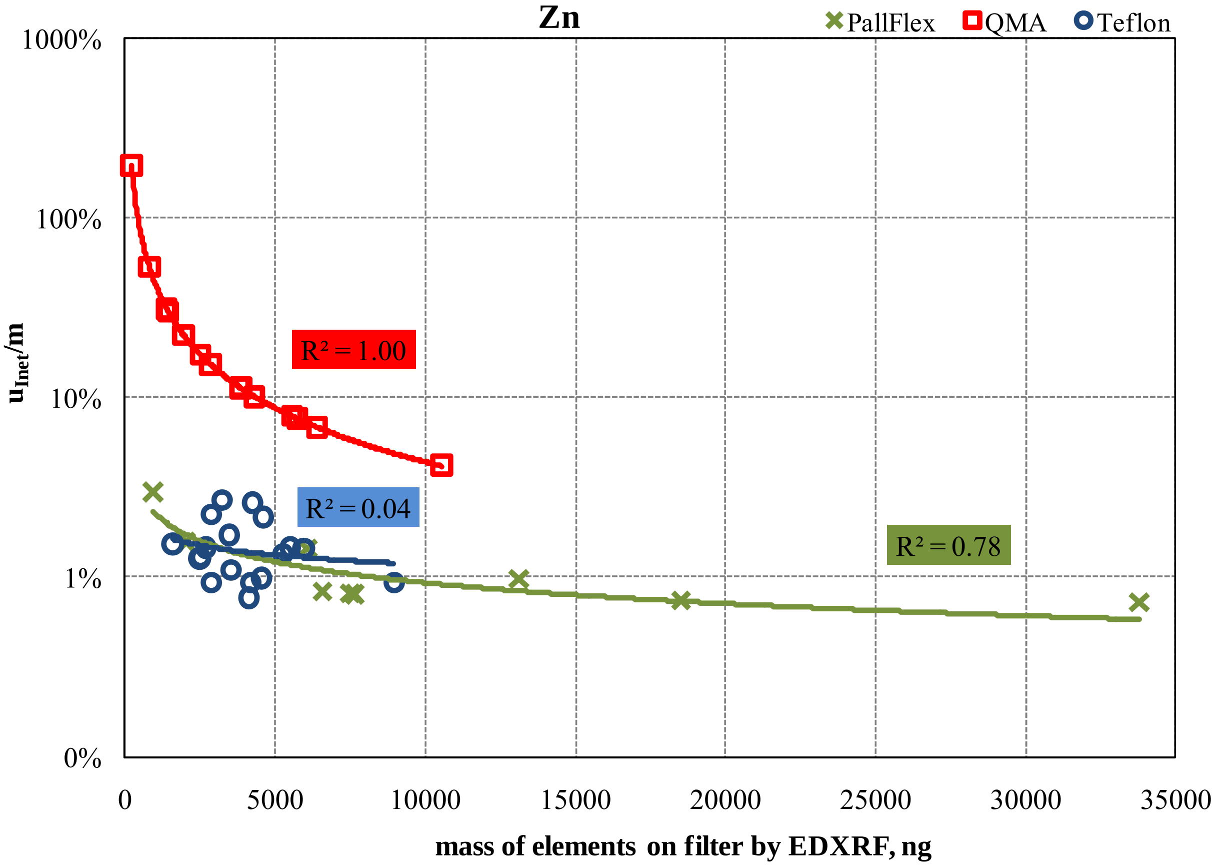

Ca
PallFlex
QMA
Teflon
35%
30%
25%
20%
15%
10%
5%
0%
u_{Inet}/m
0
20000
40000
60000
80000
100000
120000
140000
160000
180000
200000
mass of elements on filter by EDXRF, ng
R² = 1.00
R² = 0.31
R² = 0.81


Fe
PallFlex
QMA
Teflon
1000%
100%
10%
1%
0%
u_{Inet}/m
R² = 1.00
R² = 0.38
R² = 0.62
0
50000
100000
150000
200000
250000
300000
350000
400000
mass of elements on filter by EDXRF, ng

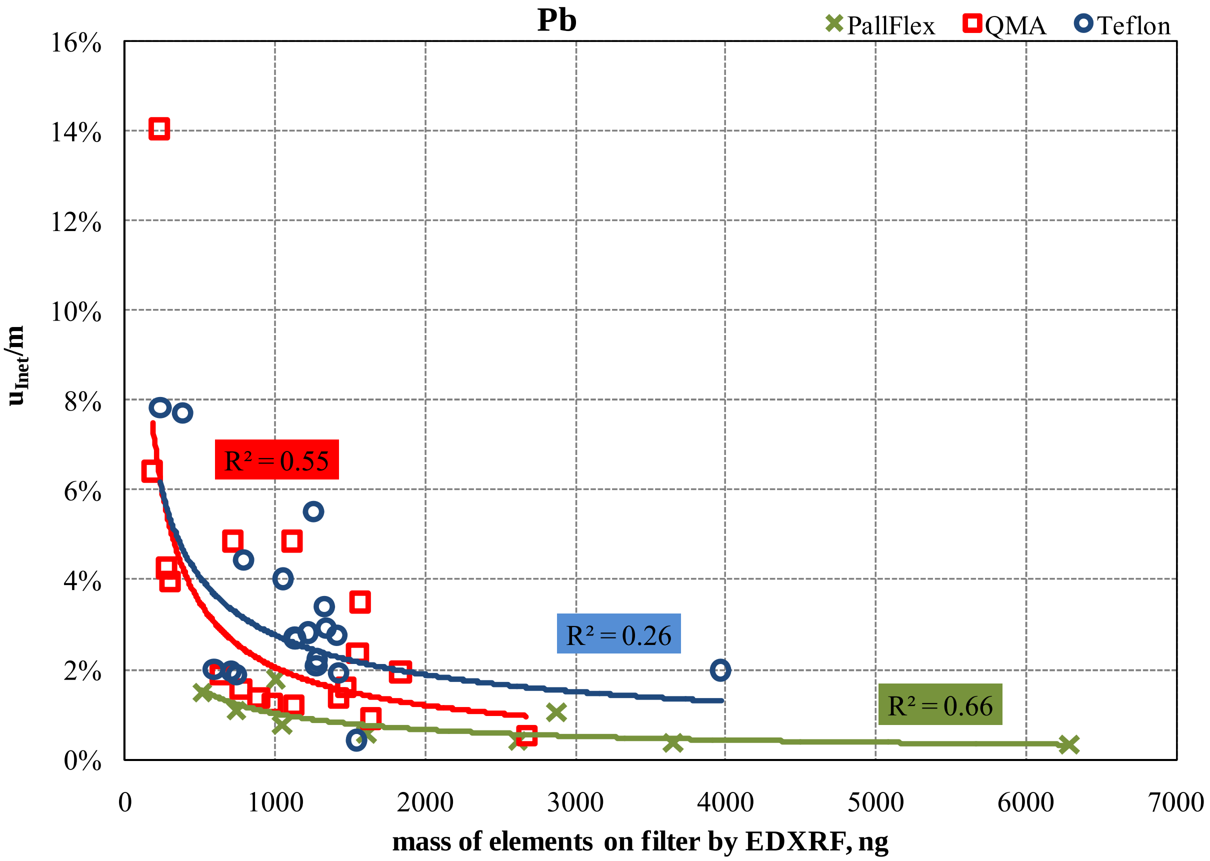

K
PallFlex
QMA
Teflon
100%
10%
1%
0%
u_{Inet}/m
R² = 1.00
R² = 0.08
R² = 0.68
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
mass of elements on filter by EDXRF, ng

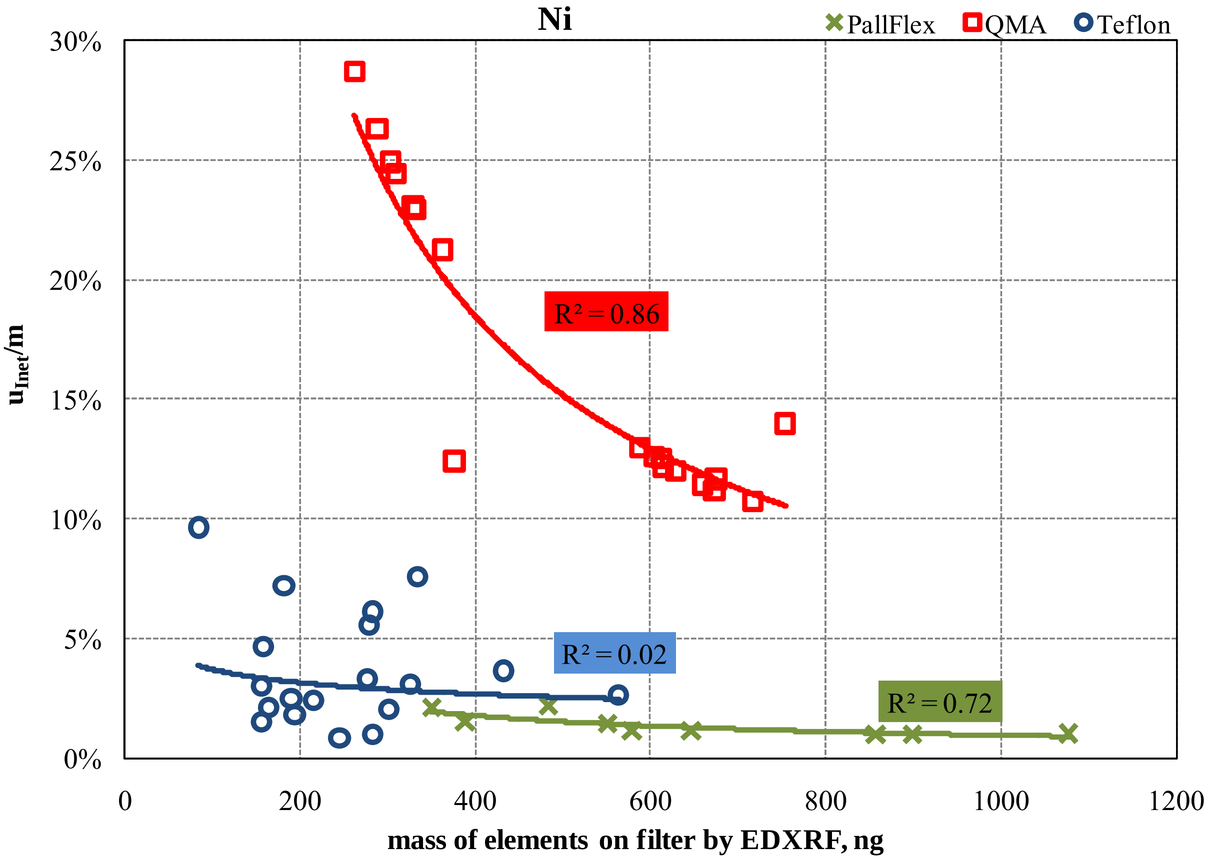


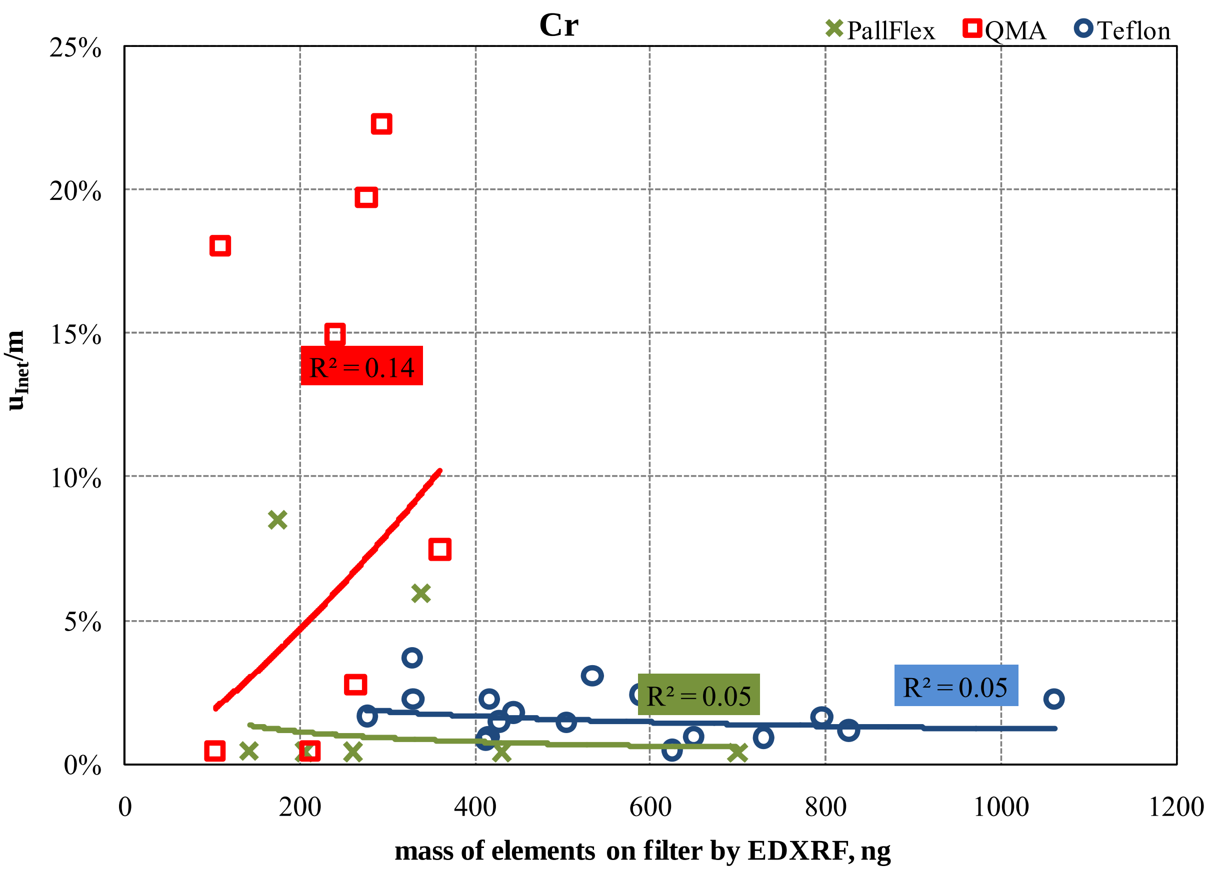
Mg
PallFlex
QMA
Teflon
8%
7%
6%
5%
4%
3%
2%
1%
0%
u_{Inet}/m
R² = 0.61
R² = 0.23
R² = 0.77
0
5000
10000
15000
20000
25000
30000
35000
mass of elements on filter by EDXRF, ng

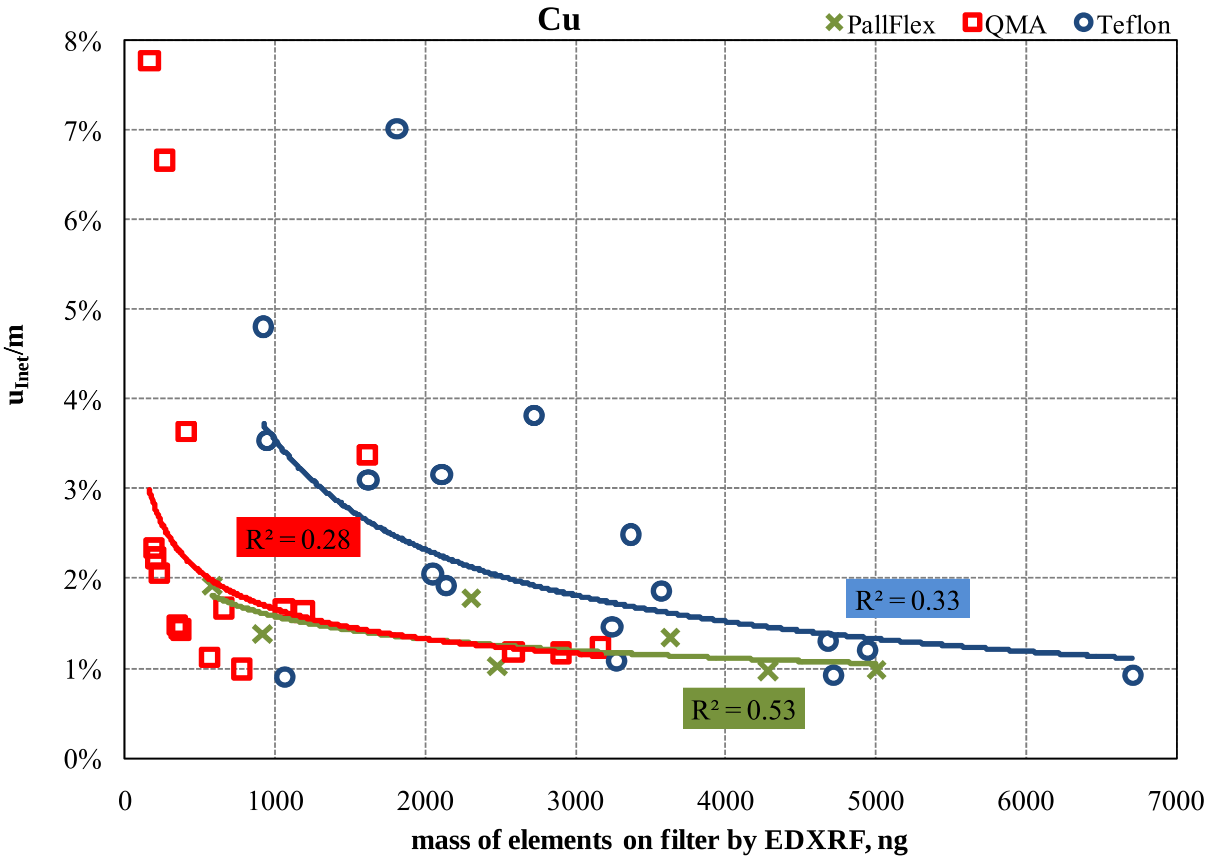


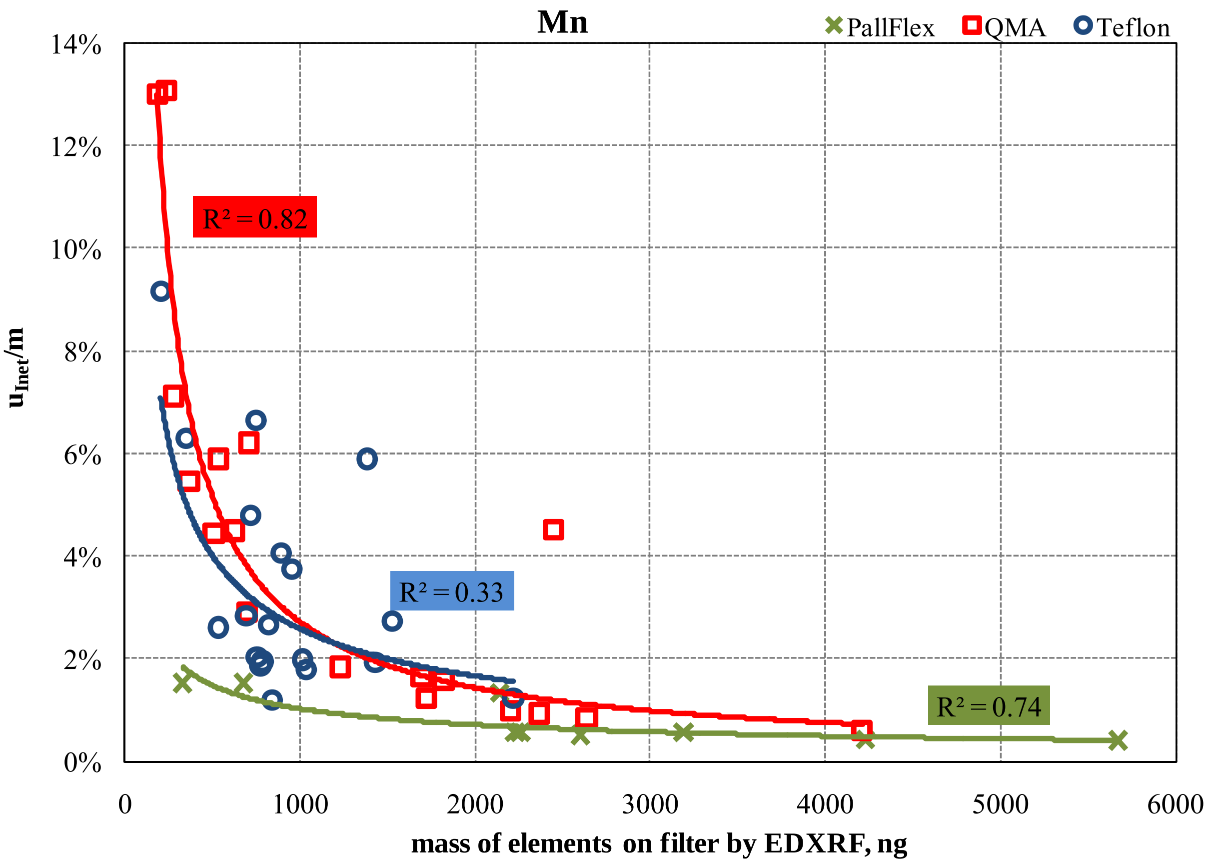
Zn
PallFlex
QMA
Teflon
1000%
100%
10%
1%
0%
u_{Inet}/m
R² = 1.00
R² = 0.04
R² = 0.78
0
5000
10000
15000
20000
25000
30000
35000
mass of elements on filter by EDXRF, ng


Pb
PallFlex
QMA
Teflon
16%
14%
12%
10%
8%
6%
4%
2%
0%
u_{Inet}/m
R² = 0.55
R² = 0.26
R² = 0.66
0
1000
2000
3000
4000
5000
6000
7000
mass of elements on filter by EDXRF, ng

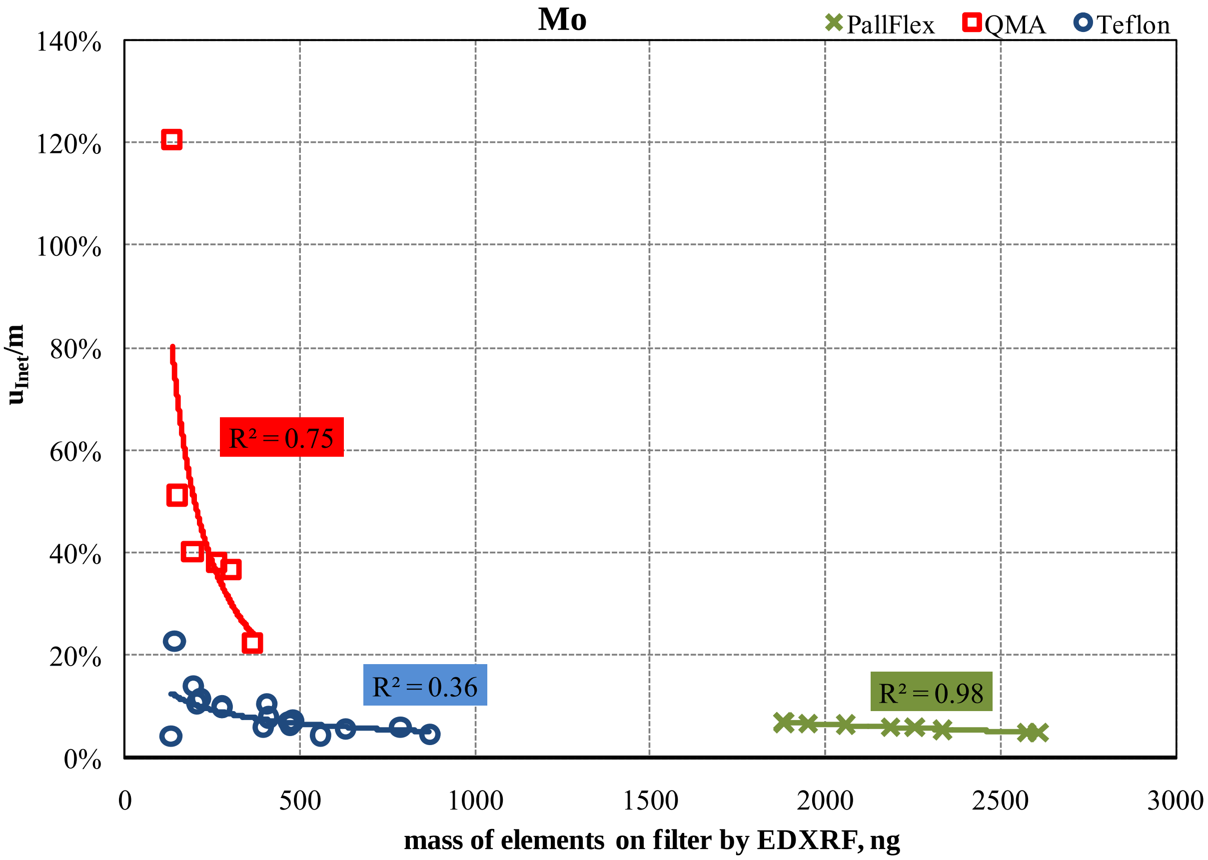

Ni
PallFlex
QMA
Teflon
30%
25%
20%
15%
10%
5%
0%
u_{Inet}/m
R² = 0.86
R² = 0.02
R² = 0.72
0
200
400
600
800
1000
1200
mass of elements on filter by EDXRF, ng


Cr
PallFlex
QMA
Teflon
25%
20%
15%
10%
5%
0%
u_{Inet}/m
R² = 0.14
R² = 0.05
R² = 0.05
0
200
400
600
800
1000
1200
mass of elements on filter by EDXRF, ng

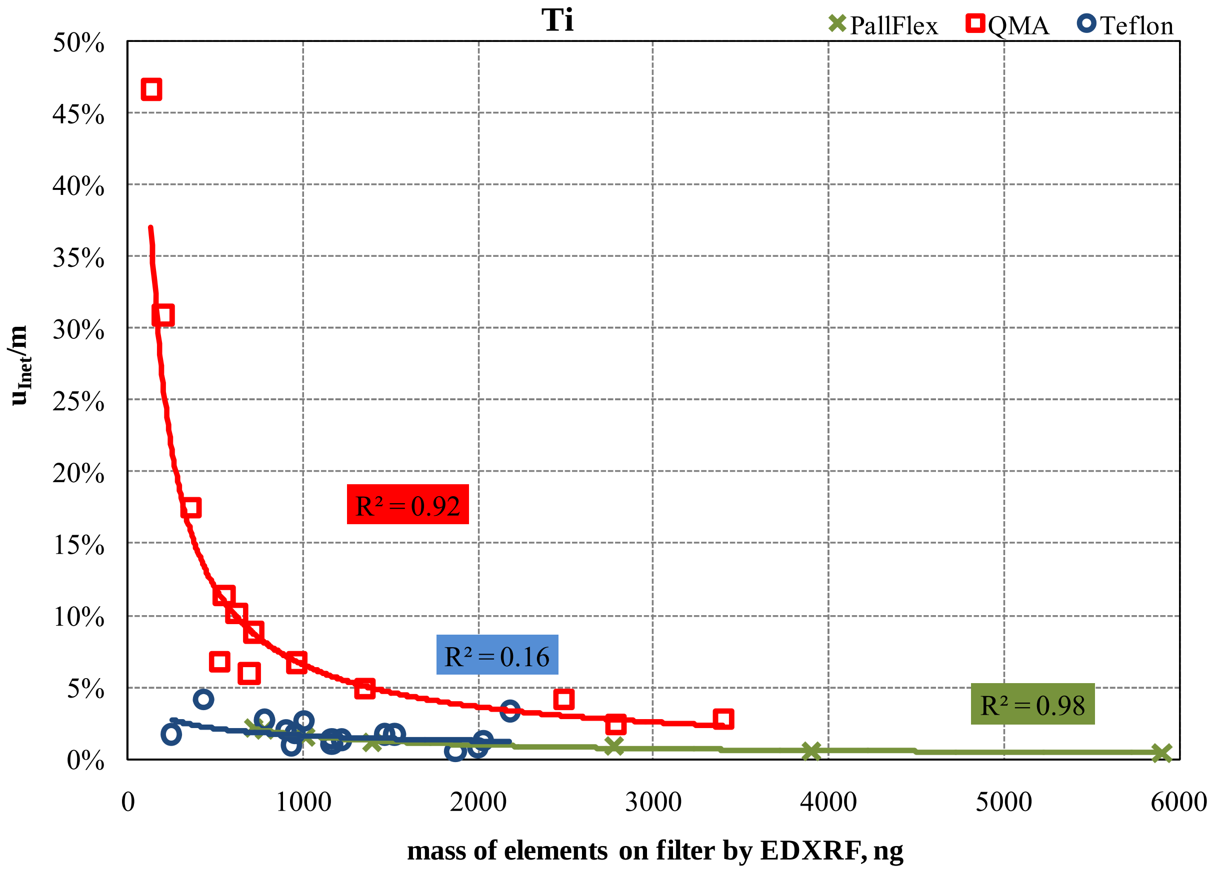

Cu
PallFlex
QMA
Teflon
8%
7%
6%
5%
4%
3%
2%
1%
0%
u_{Inet}/m
R² = 0.28
R² = 0.33
R² = 0.53
0
1000
2000
3000
4000
5000
6000
7000
mass of elements on filter by EDXRF, ng



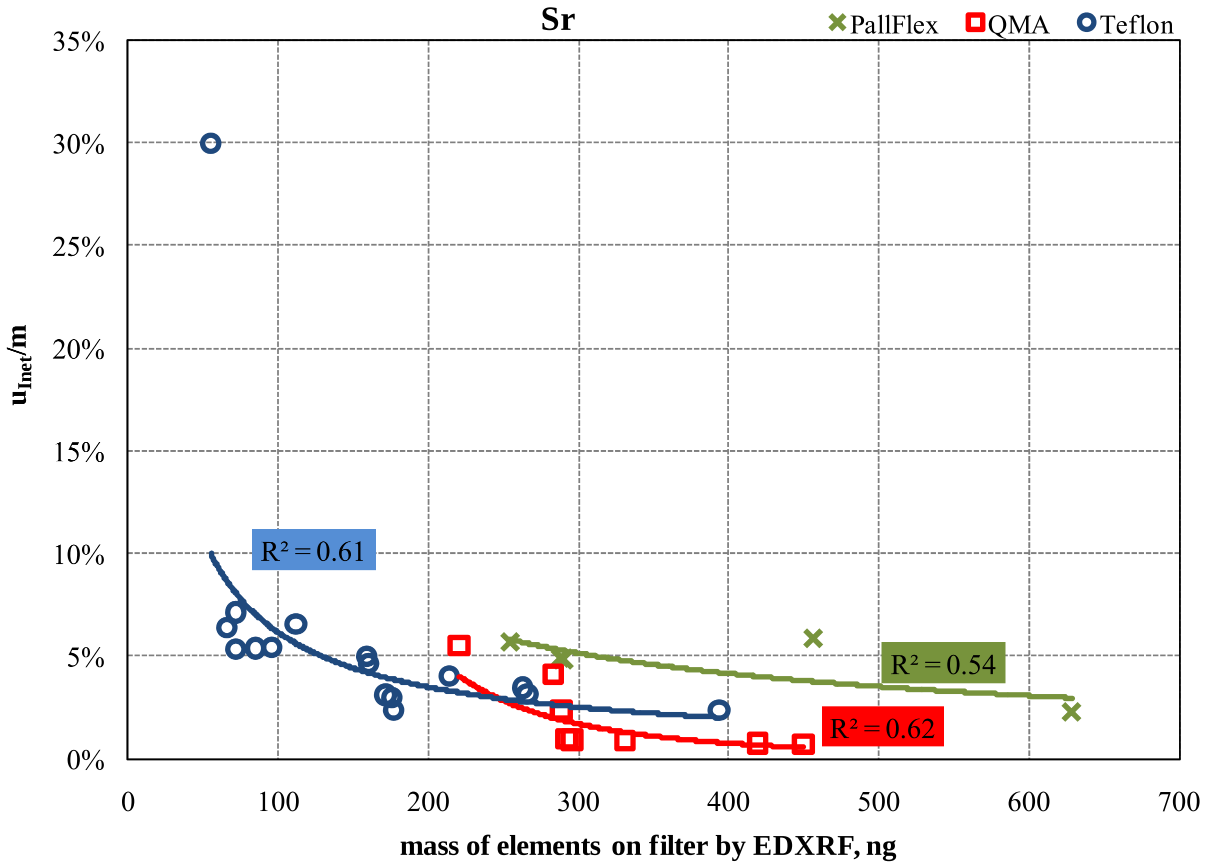
Mn
PallFlex
QMA
Teflon
14%
12%
10%
8%
6%
4%
2%
0%
u_{Inet}/m
R² = 0.82
R² = 0.33
R² = 0.74
0
1000
2000
3000
4000
5000
6000
mass of elements on filter by EDXRF, ng



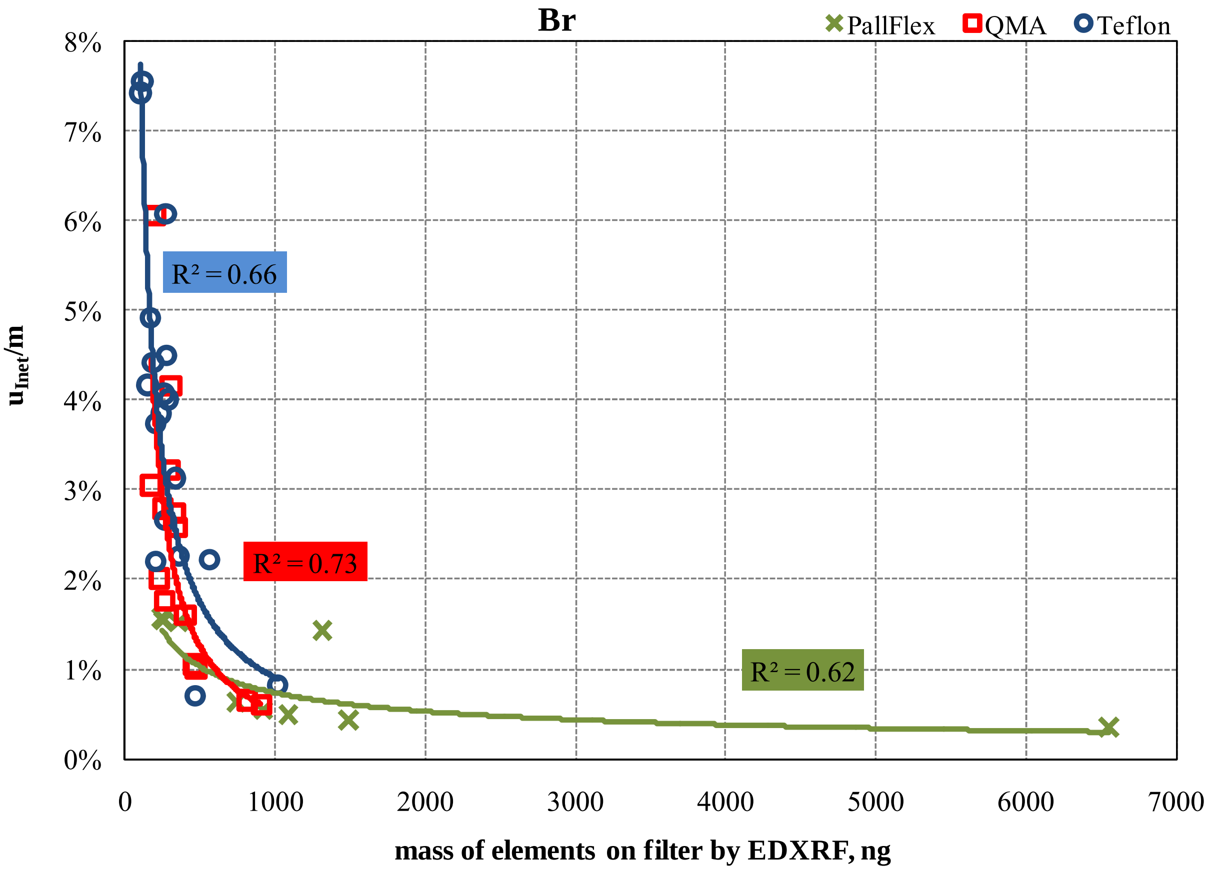
Mo
PallFlex
QMA
Teflon
140%
120%
100%
80%
60%
40%
20%
0%
u_{Inet}/m
R² = 0.75
R² = 0.36
R² = 0.98
0
500
1000
1500
2000
2500
3000
mass of elements on filter by EDXRF, ng

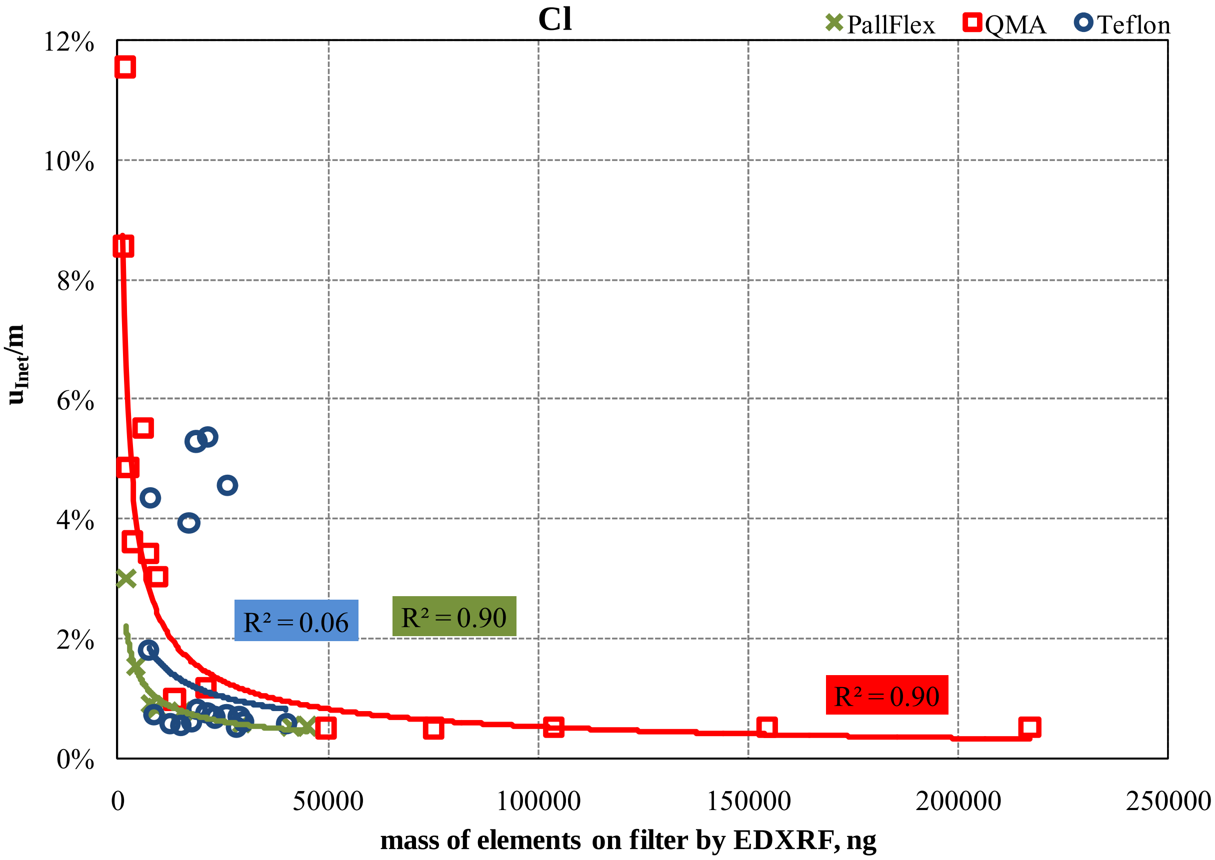


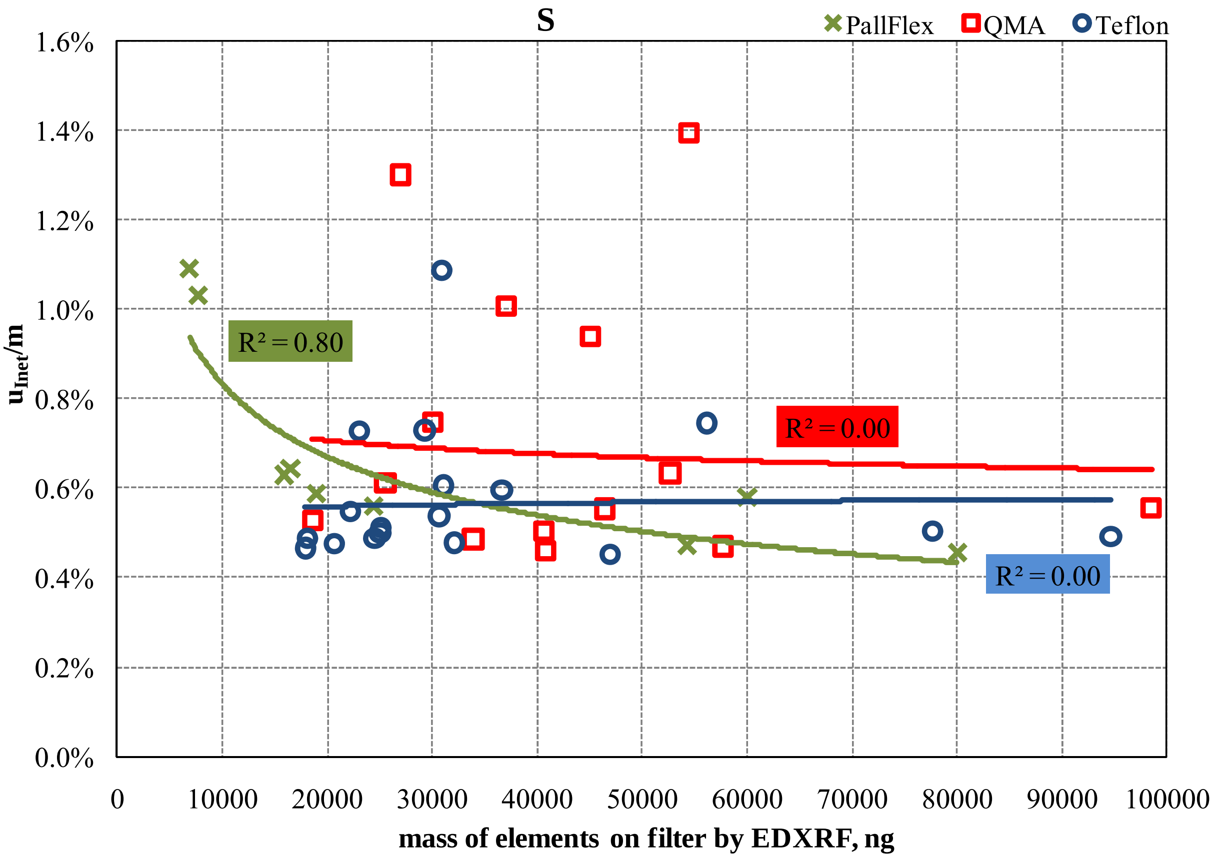
Ti
PallFlex
QMA
Teflon
50%
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%
u_{Inet}/m
R² = 0.92
R² = 0.16
R² = 0.98
0
1000
2000
3000
4000
5000
6000
mass of elements on filter by EDXRF, ng



Sr
PallFlex
QMA
Teflon
35%
30%
25%
20%
15%
10%
5%
0%
u_{Inet}/m
R² = 0.61
R² = 0.54
R² = 0.62
0
100
200
300
400
500
600
700
mass of elements on filter by EDXRF, ng


Br
PallFlex
QMA
Teflon
8%
7%
6%
5%
4%
3%
2%
1%
0%
R² = 0.66
R² = 0.73
R² = 0.62
0
1000
2000
3000
4000
5000
6000
7000
u_{Inet}/m
mass of elements on filter by EDXRF, ng


Cl
PallFlex
QMA
Teflon
12%
10%
8%
6%
4%
2%
0%
R² = 0.06
R² = 0.90
R² = 0.90
0
50000
100000
150000
200000
250000
u_{Inet}/m
mass of elements on filter by EDXRF, ng



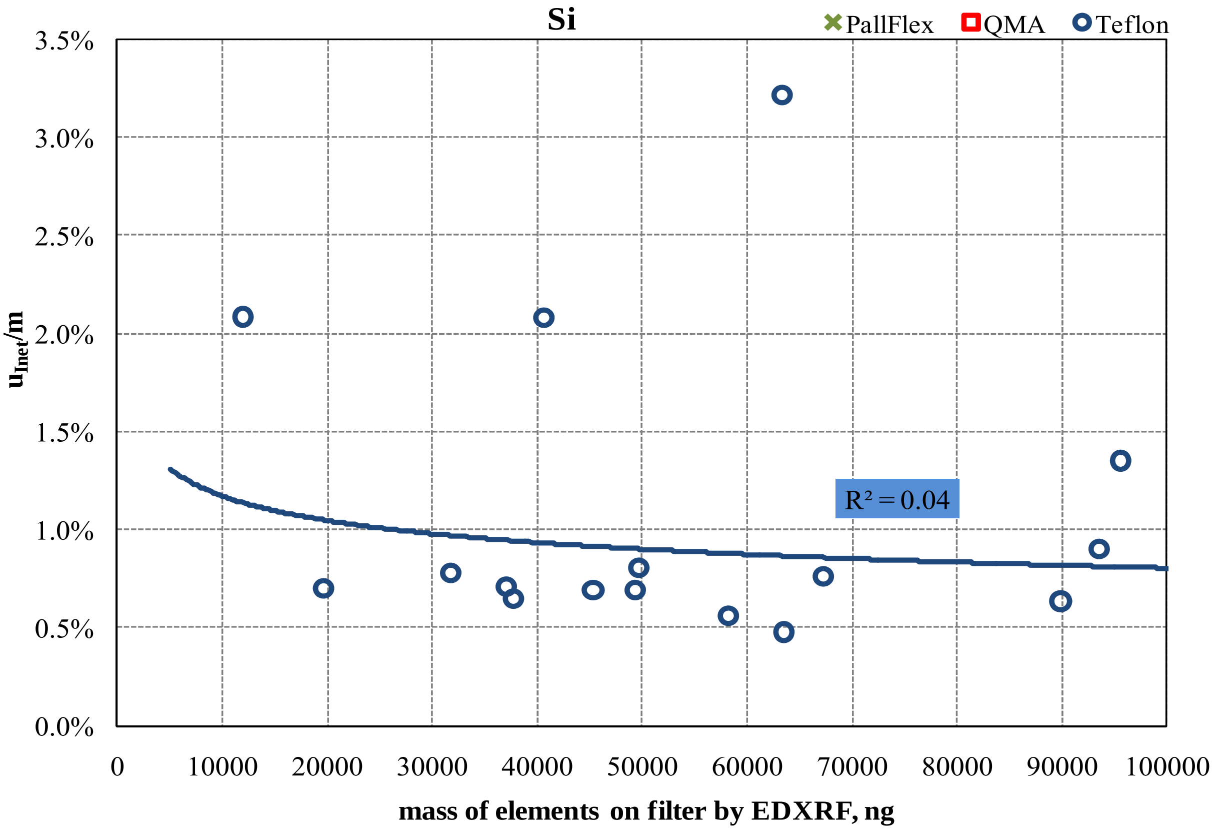


Figure 8: The variation of contribution of I_{net} and elemental mass by standardless EDXRF analysis

3.4.2 Field Uncertainty (U_{DIR}) and Data Quality Objectives

The relative expanded field uncertainties, $U_{r,DIR}$, was computed for all elements and it was compared to $U_{r,GUM}$ (see Figure 9 for PallFlex, Figure 10 for QMA and Figure 11 for Teflon filters, respectively). The elements regulated by European Directives, Ni and Pb, and by the EMEP manual[20], Cu, Cr, and Zn were analyzed in details. The relative standard uncertainties of sampling with LVS, about 2% as estimated by Gerboles et al[29], was not included in $U_{r,GUM}$ estimations because this figure was too low to significantly change $U_{r,GUM}$.

$U_{r,DIR}$ of Pb ($U_{r,DIR-Pb}$) clearly decreased with mass of Pb (m_{Pb}) for all filter types. $U_{r,GUM-Pb}$ remained constant at about 30% for all filter types whereas for the $U_{r,DIR-Pb}$ of PallFlex, QMA and Teflon filters become equal to $U_{r,GUM-Pb}$ at about 4300, 1300 and 1250 ng, respectively. One can observe that the DQO (25%) is likely to be reached at about 8000, 2000 and 2000 ng, for PallFlex, QMA and Teflon, respectively. These masses are lower than the limit value (27500 ng, assuming 55 m^3 of air sample) of the European Directive, showing that the DQO can be met. For QMA filters, r-RSS and r-Bias to $U_{r,DIR-Pb}$ ranged between 40-80% and 20-60%. r-RSS to $U_{r,DIR-Pb}$ decreased with m_{Pb} whereas the contribution of bias was the opposite. For Teflon and PallFlex filters, the dominant contribution to $U_{r,DIR-Pb}$ (60 to 95%) came from the bias that increased with m_{Pb}.

For Teflon filters, $U_{r,DIR-Ni}$ decreased with m_{Ni}. $U_{r,DIR}$-Ni for Teflon filters at the European limit value (1100 ng for 55 m^3 of sampled volume), was estimated to be 20 % by extrapolation, a figure lower than the DQO (40%). However, more tests would be required at higher Ni masses to confirm this observation. The relative contribution of RSS to (r-RSS) and of the bias (r-Bias) to $U_{r,DIR-Ni}$ ranged between 75-100% and 0-25%, respectively. r-RSS to $U_{r,DIR-Ni}$ increased with m_{Ni} whereas r-Bias to $U_{r,DIR-Ni}$ decreased. At low m_{Ni}, $U_{r,DIR-Ni}$ was found much higher than $U_{r,GUM-Ni}$, meaning that Equation 6 does not cover all the uncertainty sources for low m_{Ni}.

For PallFlex, increasing m_{Ni} leads to closer values of $U_{r,DIR-Ni}$ and $U_{r,GUM-Ni}$. However, at the LV of the European Directive, the DQO could not be met for PallFlex. r-RSS to $U_{r,DIR-Ni}$ and r-Bias to $U_{r,DIR-,Ni}$ ranged between 30-95% and 5-70%, respectively. r- RSS to $U_{r,DIR-Ni}$ increased with m_{Ni} whereas r-Bias was the opposite.

The EMEP manual[20] states some metals, Cd and Pb as first priority, then Ni, As, Cr, Cu and Zn as second priority plus some cations (Na, Mg, Ca, and K) that should be monitored at rural sites. The EMEP manual states a DQO of 25 % for these measurements, but without limit values to which the DQO applies.

It is likely that the standardless EDXRF analysis cannot meet the EMEP-DQO for Cr for whatever filter type since both $U_{r,DIR-Cr}$ and $U_{r,GUM-Cr}$ were always higher than 25 %. Moreover, $U_{r,DIR-Cr}$ was always higher than $U_{r,GUM-Cr,}$ indicating that for Cr, an unknown source of uncertainty was not taken into account in Equation 6 or more likely, that the well known difficulty of Cr digestion resulted in underestimation of Cr ICP-MS analysis (Gerboles et al., 2011[29]) specially with the PallFlex filters. The bias was the overwhelming contributor to $U_{r,DIR-Cr}$ for PallFlex . For Teflon and QMA filters, r-RSS to $U_{r,DIR-Cr}$ (ranging between 10-90%) decreased with m_{Cr} whereas r-Bias to $U_{r,DIR-Cr}$ was the opposite.

For Teflon filters, $U_{r,GUM-Cu}$ remained steady at about 28%. $U_{r,DIR-Cu}$ sharply dropped in from 150 % at 200 ng of Cu that bottomed out at about 30 % at 3800 ng of Cu where $U_{r,DIR-Cu}$ and $U_{r,GUM-Cu}$ lines crossed each others. The DQO of 25 % was met at about 4500 ng. At m_{Cu} lower than 2500 ng, the major contribution to $U_{r,DIR-Cu}$, came from RSS (see Figure 11) while the bias became the key contributor to $U_{r,DIR-Cu}$ (up to 95 %) for m_{Cu} higher than 2500 ng. For PallFlex filters, $U_{r,GUM-Cu}$ slightly decreased from 55 to 35 % on the whole m_{Cu} range while $U_{r,DIR-Cu}$ had a rapid drop from 300 % down to 40 % at 3700 ng of m_{Cu} where $U_{r,DIR-Cu}$ was equal to $U_{r,GUM-Cu}$. At higher m_{Cu} values, $U_{r,DIR-Cu}$ kept on slightly decreasing down to 20 %. The DQO of 25 % was met for m_{Cu} higher than 4500 ng. $U_{r,DIR-Cu}$ completely depended on the bias. At lower m_{Cu}, better results were obtained for QMA filters than for PallFlex and Teflon filters. For QMA, $U_{r,GUM-Cu}$ slightly decreased (from 32 to 27%) while $U_{r,DIR-Cu}$

had a rapid drop from 220 % down to 30 % at about 1750 ng of m_{Cu} where $U_{r,DIR-Cu}$ was equal to $U_{r,GUM-Cu}$. The DQO of 25 % was met for m_{Cu} at about 2000 ng. For QMA, at m_{Cu} less than 1500 ng, the major contribution to $U_{r,DIR-Cu}$ came from the random sources (see Figure 10) while the bias became the key contributor (up to 80 %) to $U_{r,DIR-Cu}$ for higher m_{Cu}.

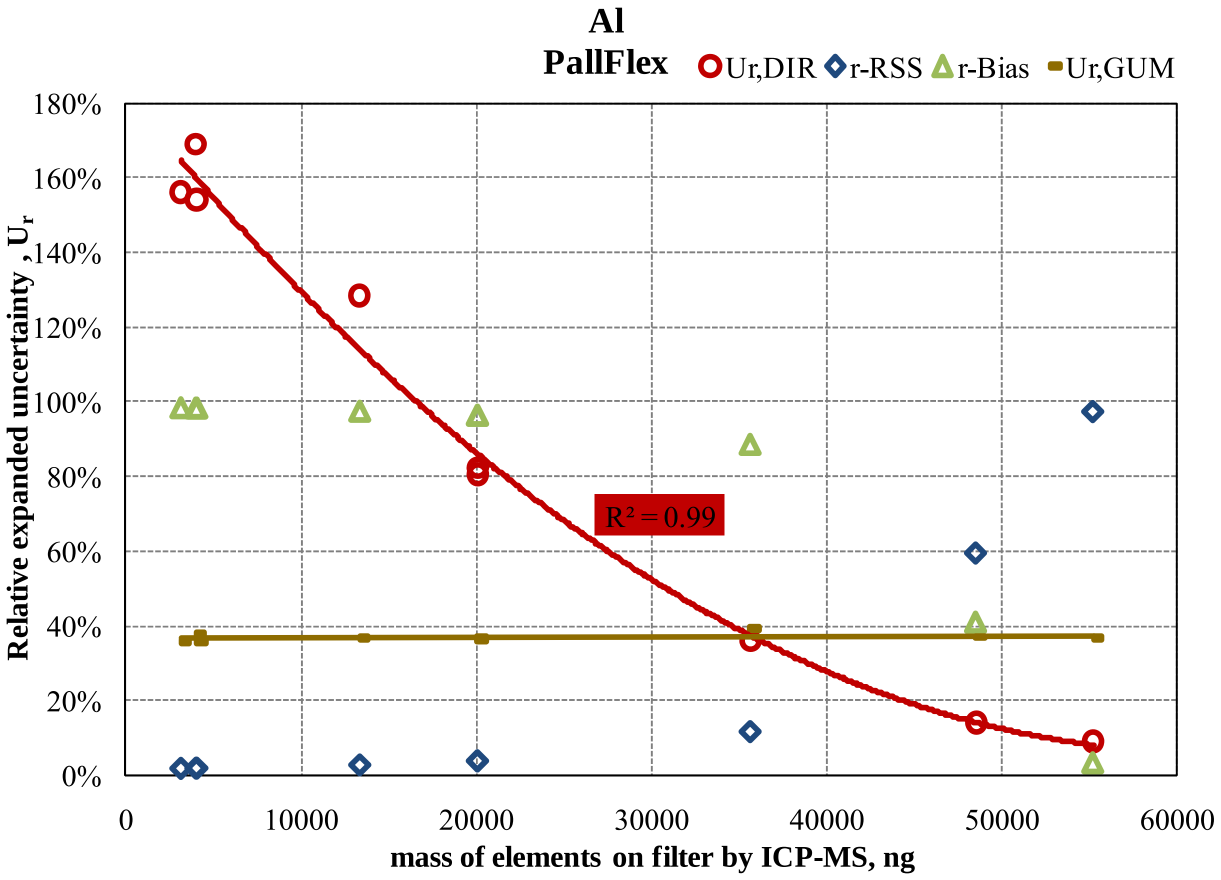
For Teflon filters, $U_{r,DIR-Zn}$ and $U_{r,GUM-Zn}$ were found to be constant over the whole mass range with a difference of about 10 % ($U_{r,DIR-Zn}$ higher than $U_{r,GUM-Zn}$). Actually, for Zn, RD and RAD were found independent from m_{Zn}, with values around 25 % (see Figure 5) and 20±20% (Figure 6), respectively. This suggested that systematic and random errors were present in the Zn measurements. The sample to blank ratio (S/B) for Zn as measured by ICP-MS was particularly low (1.0-1.8, min-max). It was induced by a blank contamination, which led to $U_{r,DIR-Zn}$ around 35-40%. Lower blanks and thus, higher S/B of ICP-MS for Zn measurements are likely to decrease $U_{r,DIR-Zn}$. At low m_{Zn}, both r-RSS and r-Bias to $U_{r,DIR-Zn}$ were about 50%. The contribution of RSS to $U_{r,DIR-Zn}$ decreased with m_{Zn} whereas r-Bias to $U_{r,DIR-Zn}$ (50-95%) was the opposite. For QMA filters, $U_{r,DIR-Zn}$ and $U_{r,GUM-Zn}$ decreased with m_{Zn}. $U_{r,DIR-Zn}$ became lower than $U_{r,GUM-Zn}$ for m_{Zn} at about 9500 ng. However, $U_{r,DIR-Zn}$ (28%) was not sufficient to meet the EMEP-DQO. It is likely to be met at higher m_{Zn}. r-RSS to $U_{r,DIR-Zn}$ (ranging between 70-100%) increased with m_{Zn} whereas the r-Bias to $U_{r,DIR-Zn}$ was the opposite. For PallFlex filters, $U_{r,GUM-Zn}$ was estimated at about 30% whereas $U_{r,DIR-Zn}$ decreased with m_{Zn}. For m_{Zn} higher than 12500 ng, $U_{r,DIR-Zn}$ was equal or lower than $U_{r,GUM-Zn}$. The EMEP-DQO was met at about 15000 ng. However, for m_{Zn} at about 30000 ng, $U_{r,DIR-Zn}$ increased up to 30%. More tests between 15000 and 30000 ng are required to check the compliance with EMEP-DQO. The range of r-RSS and r-Bias to $U_{r,DIR-Zn}$ were between 50 and 100%. r-RSS to $U_{r,DIR-Zn}$ decreased with m_{Zn} whereas r-Bias to $U_{r,DIR-Zn}$ was the opposite.

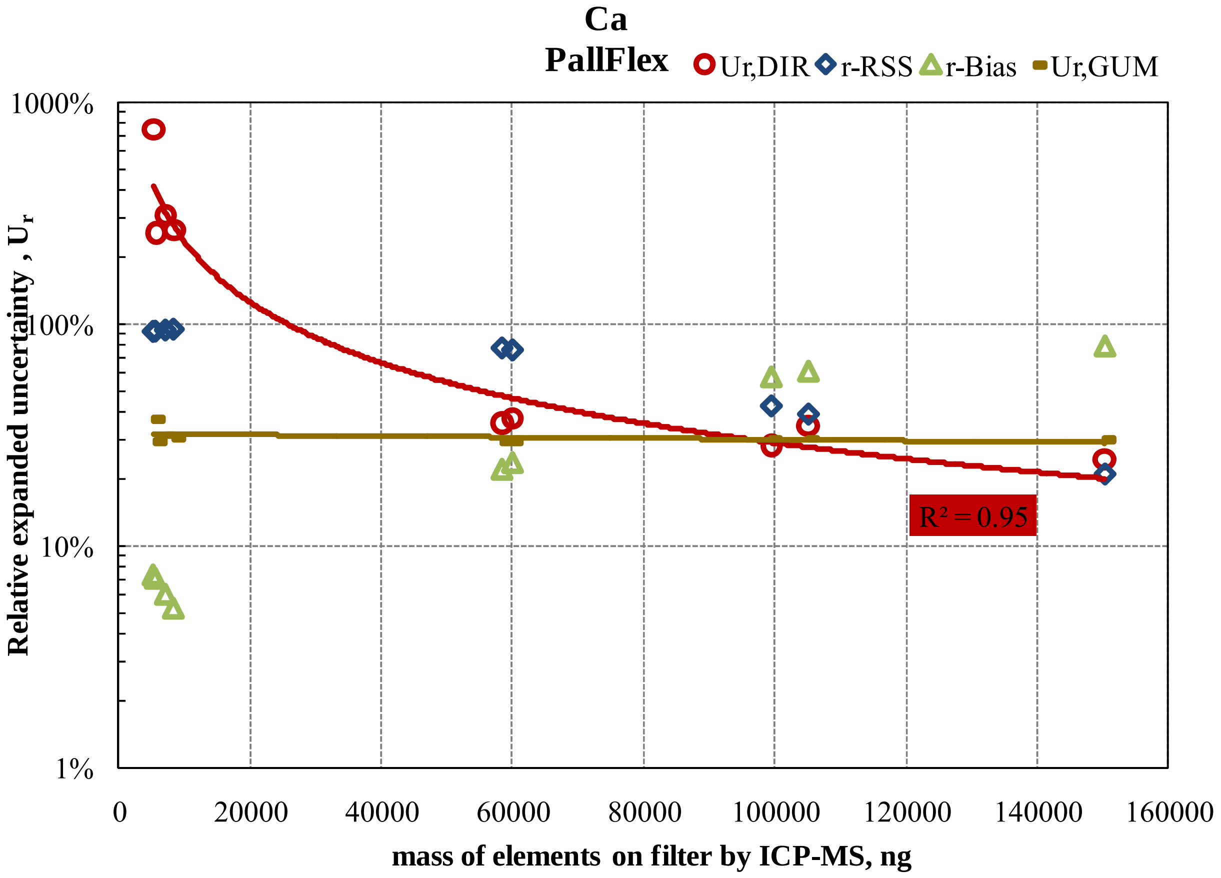
For QMA and Teflon filters, $U_{r,DIR-Mn}$ was lower than $U_{r,GUM-Mn}$ for m_{Mn} higher than 1100 and 1400 ng, respectively. For PallFlex, there is a clear trend showing a sharp decrease of $U_{r,DIR-Mn}$ for m_{Mn} till 2000 ng that bottomed out at about 35%. More samples with m_{Mn} higher than 2000 ng would be needed to clarify the pattern.

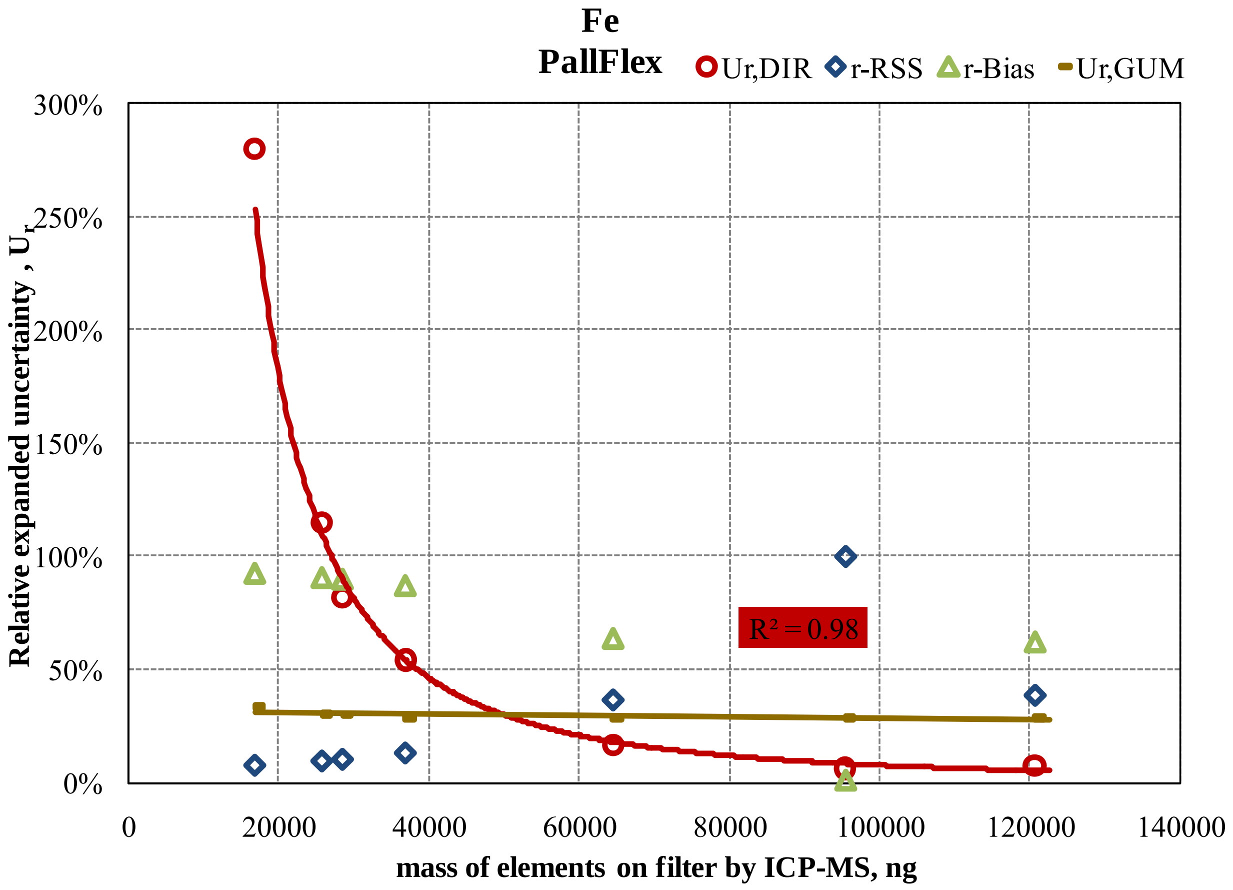
For Teflon filters, $U_{r,DIR-Mo}$ decreased with m_{Mo} and it became close to $U_{r,GUM-Mo}$ for m_{Mo} higher than 450 ng. For PallFlex filters, $U_{r,GUM-Mo}$ remained always lower than $U_{r,DIR-Mo}$ which decreased with m_{Mo}. For Ti, $U_{r,DIR}$ was always higher than $U_{r,GUM}$ for QMA and PallFlex. For Teflon filters, $U_{r,DIR-Ti}$ was lower than $U_{r,GUM-Ti}$ at about 2000 ng. One may note the presence of a strange filter with a huge $U_{r,DIR-Ti}$ value caused by a random difference between ICP-MS and EDXRF.

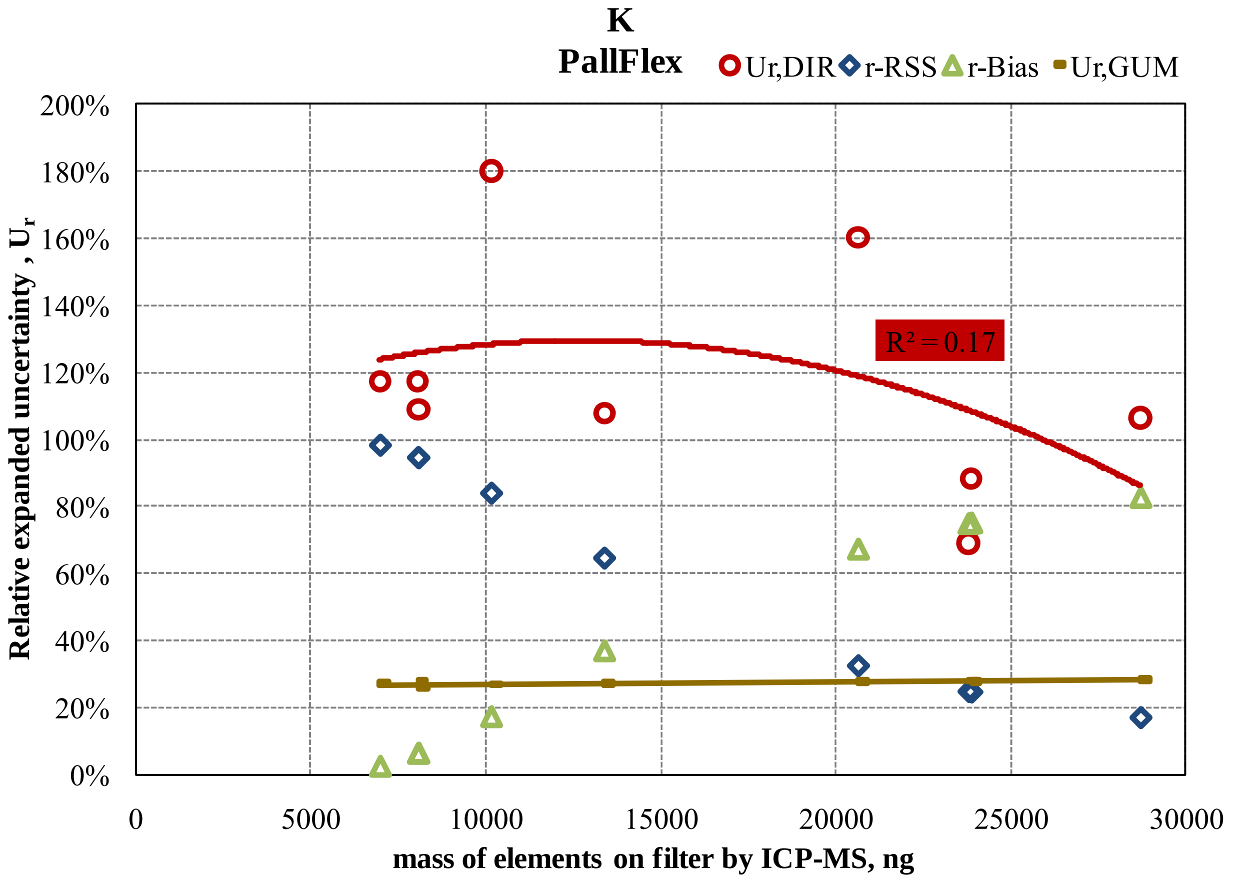
For Al, Ca and Fe, $U_{r,DIR}$ decreased to the value of $U_{r,GUM}$ at some thresholds of elemental masses. These thresholds masses were lower for Teflon filters than for quartz. This can be attributed to more impurities of those elements in quartz filters. Furthermore, the thresholds of elemental masses were lower for PallFlex filters than for QMA ones. This is consistent with the lower EDXRF-MDLs given in Table 3 for these filter types. This pattern may occur because of the borosilicate glass content in the filter material. The thresholds did not appear for Mg and K for all types of filters.

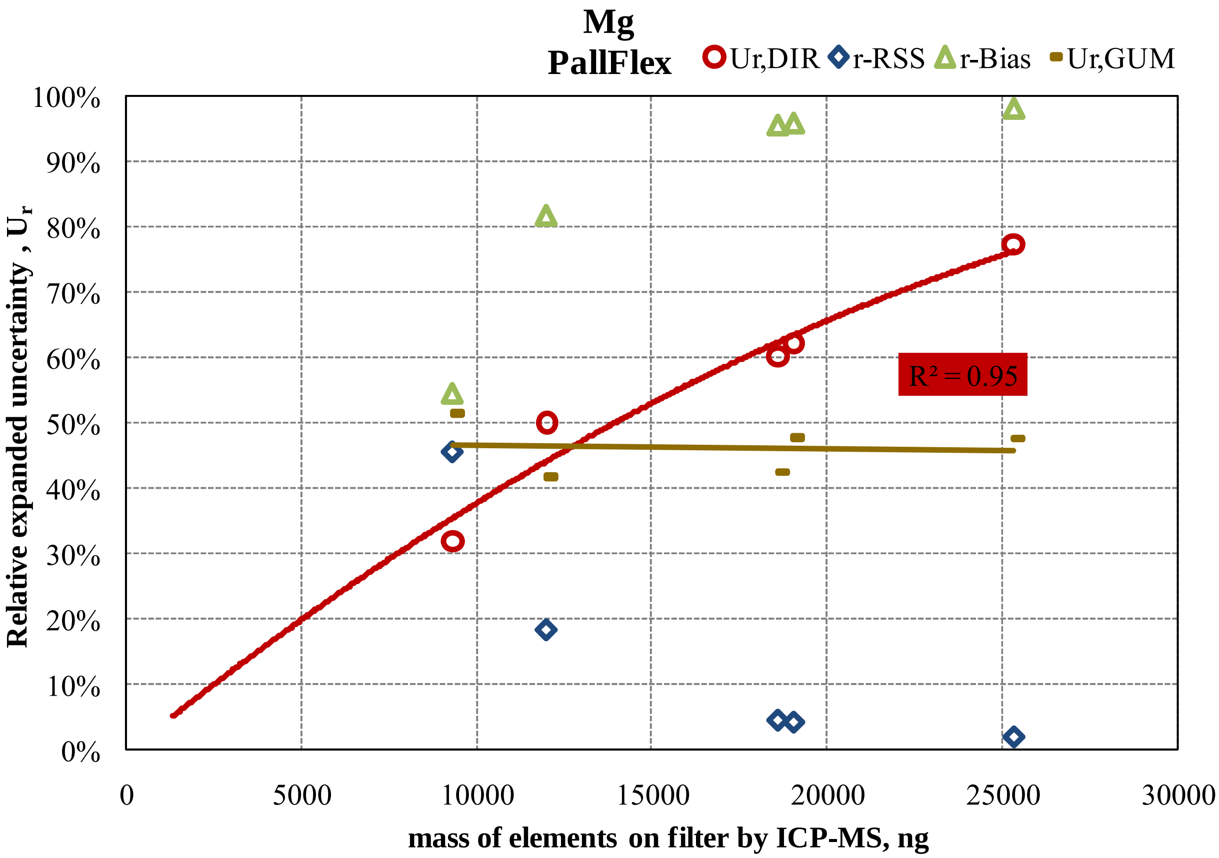
Conversely to the measurement uncertainties which were found to be independent from elemental masses except for Ca, Fe, K, Zn, Mn, Ni, Ti (QMA), Cu and Ti (PallFlex) and Mo (Teflon), the field ones ($U_{r,DIR}$) always changed with the elemental masses. For low masses, $U_{r,DIR}$ was calculated higher than $U_{r,GUM}$, meaning that the GUM model equation did not cover all the influencing factors.

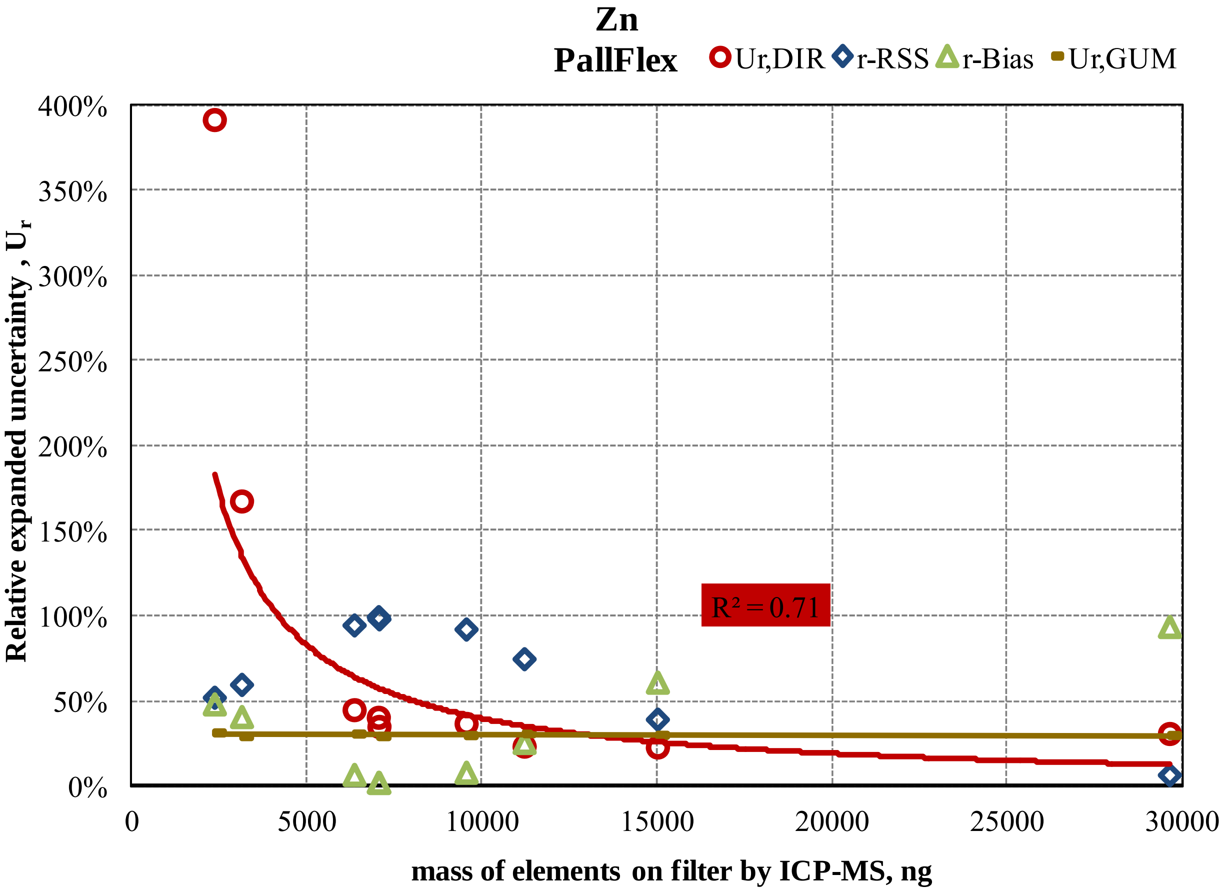

Al
PallFlex
Ur,DIR
r-RSS
r-Bias
Ur,GUM
Relative expanded uncertainty , U_r
180%
160%
140%
120%
100%
80%
60%
40%
20%
0%
0
10000
20000
30000
40000
50000
60000
mass of elements on filter by ICP-MS, ng
R² = 0.99

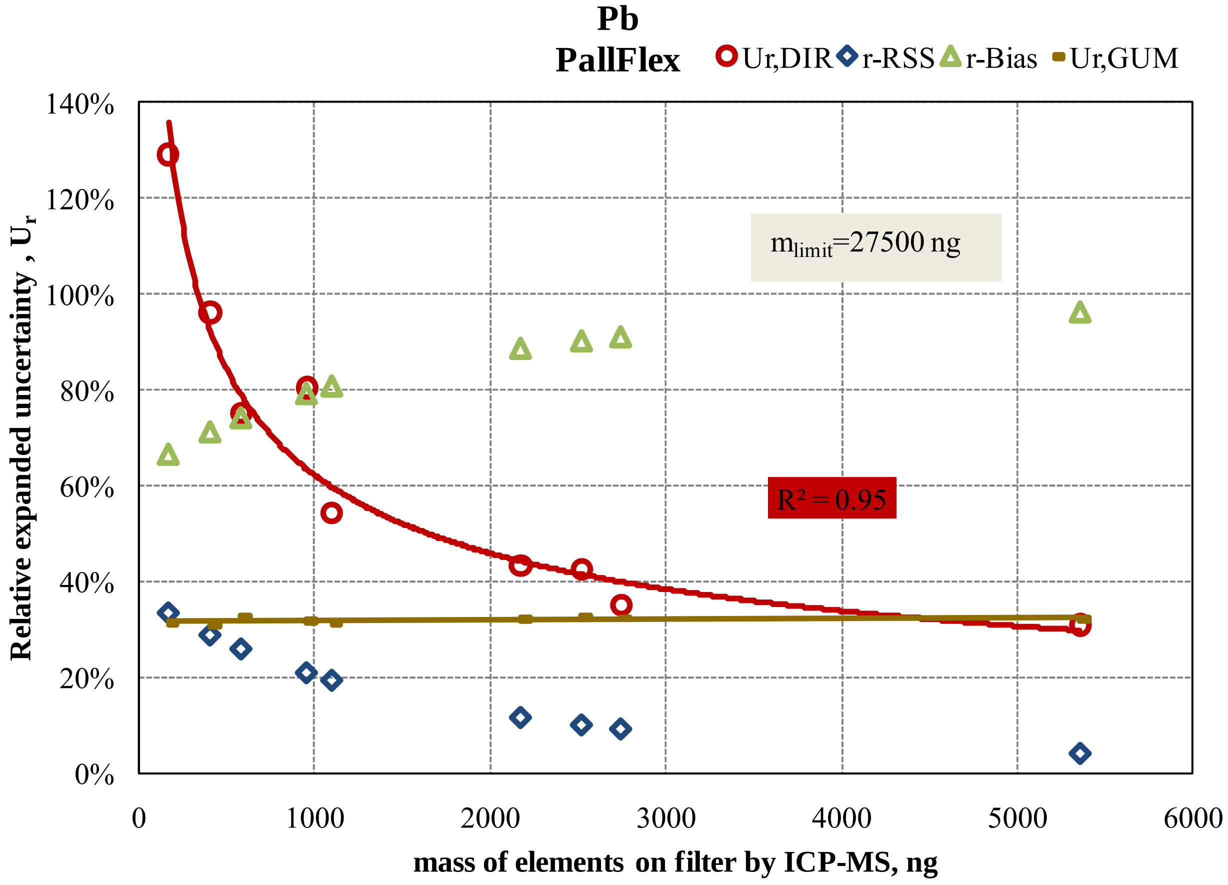

Ca
PallFlex
Ur,DIR
r-RSS
r-Bias
Ur,GUM
Relative expanded uncertainty , U_r
1000%
100%
10%
1%
0
20000
40000
60000
80000
100000
120000
140000
160000
mass of elements on filter by ICP-MS, ng
R² = 0.95


Fe
PallFlex
Ur,DIR
r-RSS
r-Bias
Ur,GUM
Relative expanded uncertainty , U_r
300%
250%
200%
150%
100%
50%
0%
R² = 0.98
0
20000
40000
60000
80000
100000
120000
140000
mass of elements on filter by ICP-MS, ng

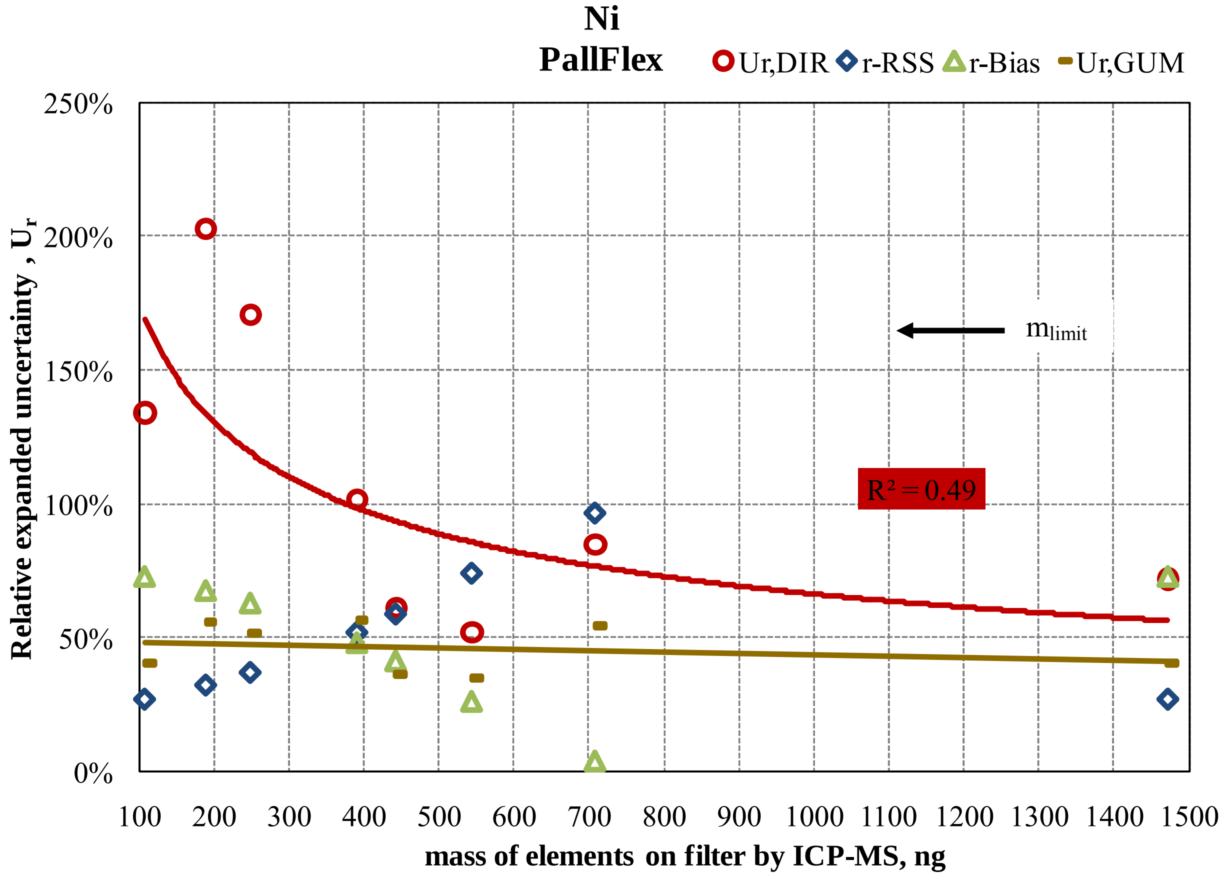

K
PallFlex
Ur,DIR
r-RSS
r-Bias
Ur,GUM
Relative expanded uncertainty , U_r
200%
180%
160%
140%
120%
100%
80%
60%
40%
20%
0%
R² = 0.17
0
5000
10000
15000
20000
25000
30000
mass of elements on filter by ICP-MS, ng


Mg
PallFlex
Ur,DIR
r-RSS
r-Bias
Ur,GUM
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Relative expanded uncertainty , U_r
R² = 0.95
0
5000
10000
15000
20000
25000
30000
mass of elements on filter by ICP-MS, ng

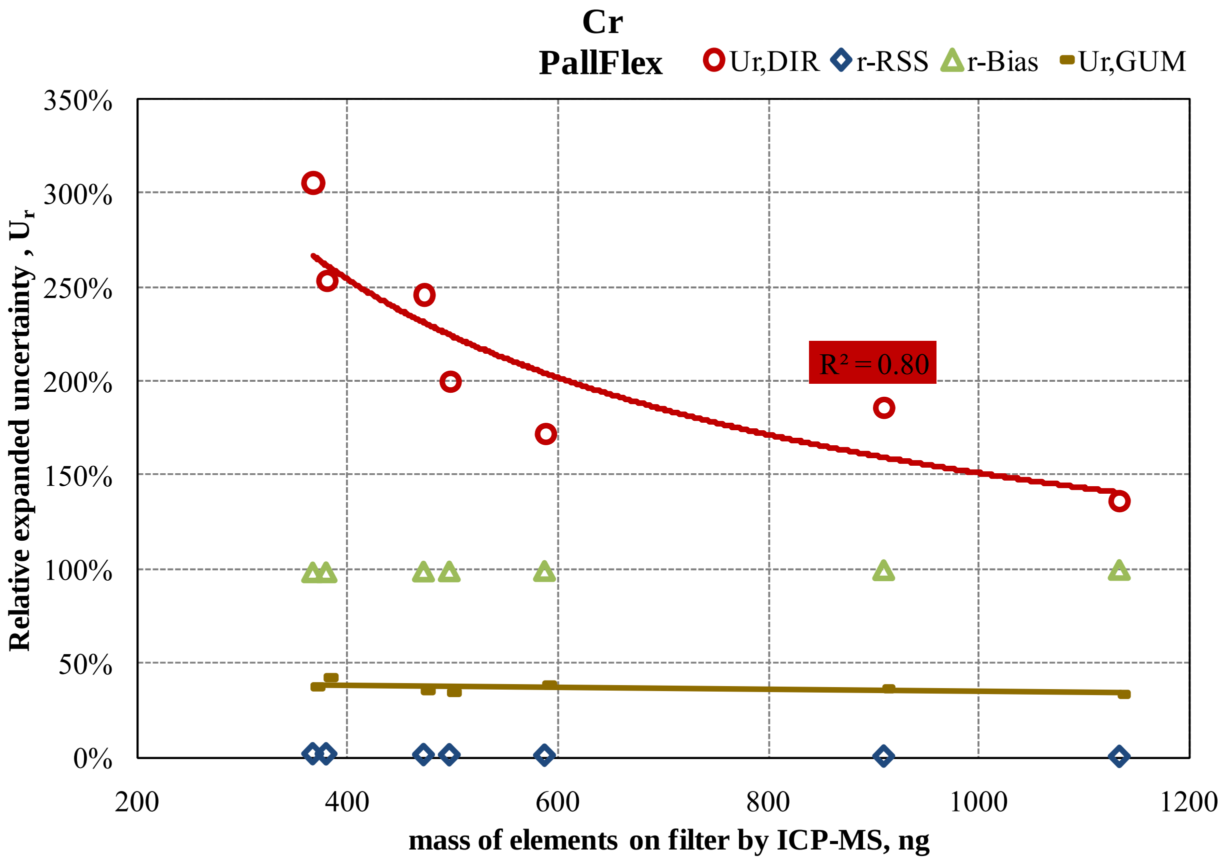

Zn
PallFlex
Ur,DIR
r-RSS
r-Bias
Ur,GUM
400%
350%
300%
250%
200%
150%
100%
50%
0%
Relative expanded uncertainty , U_r
R² = 0.71
0
5000
10000
15000
20000
25000
30000
mass of elements on filter by ICP-MS, ng

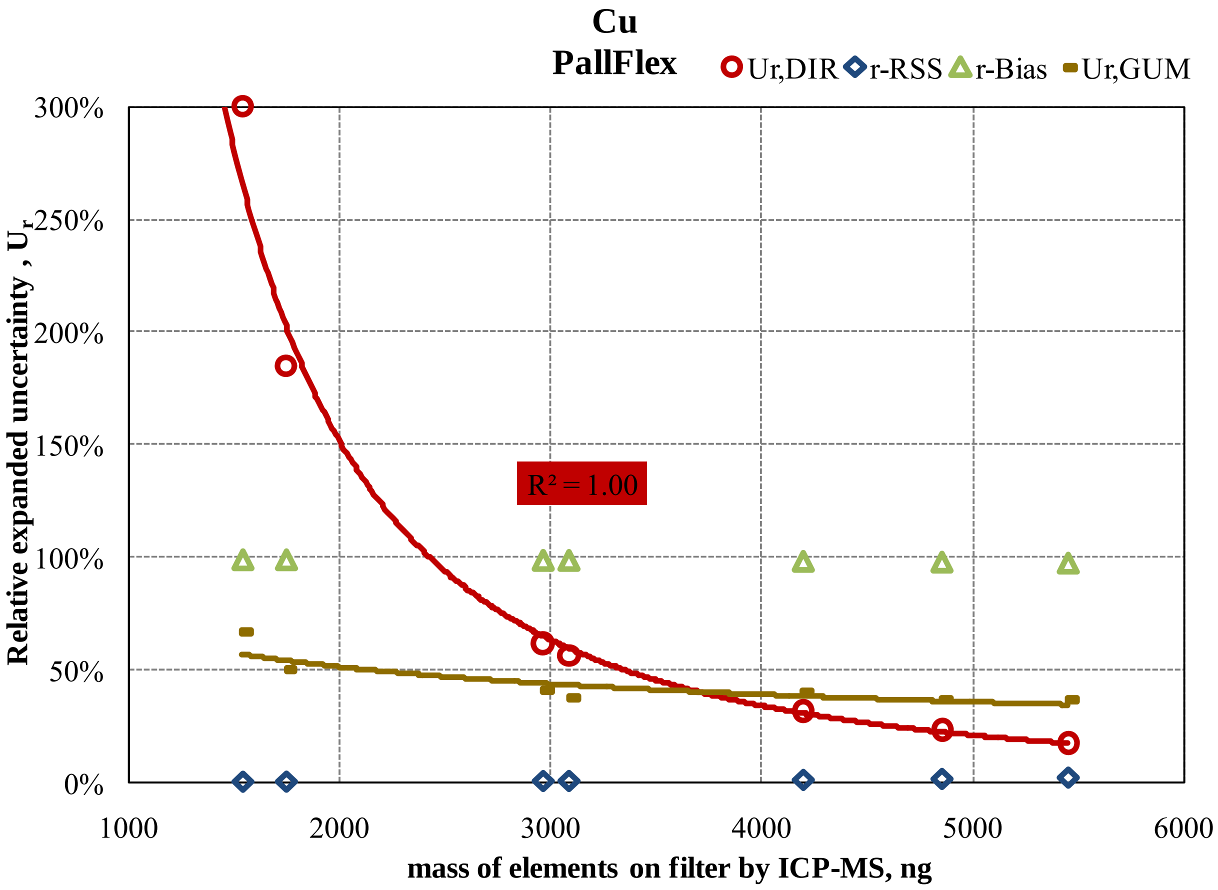


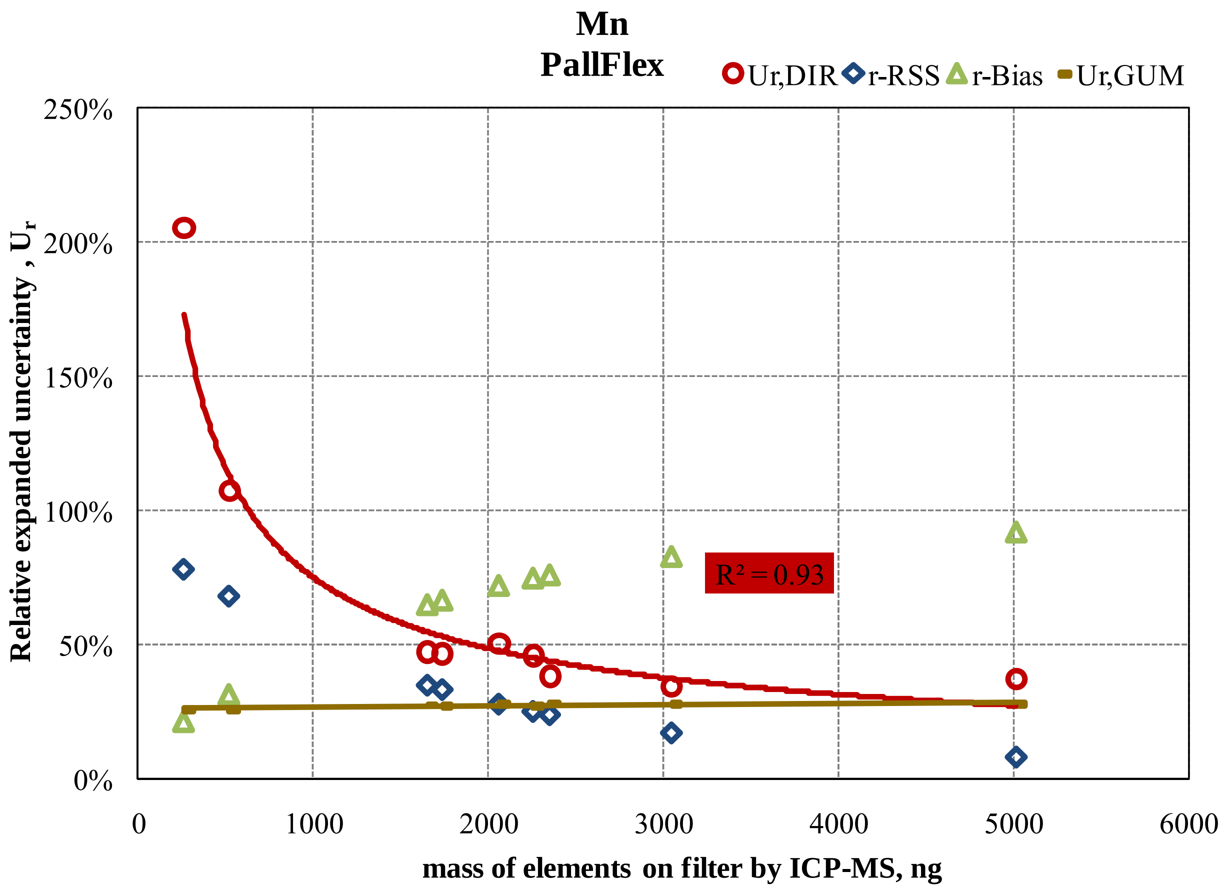
Pb
PallFlex
Ur,DIR
r-RSS
r-Bias
Ur,GUM
m_{limit}=27500 ng
R² = 0.95
Relative expanded uncertainty , U_r
140%
120%
100%
80%
60%
40%
20%
0%
0
1000
2000
3000
4000
5000
6000
mass of elements on filter by ICP-MS, ng

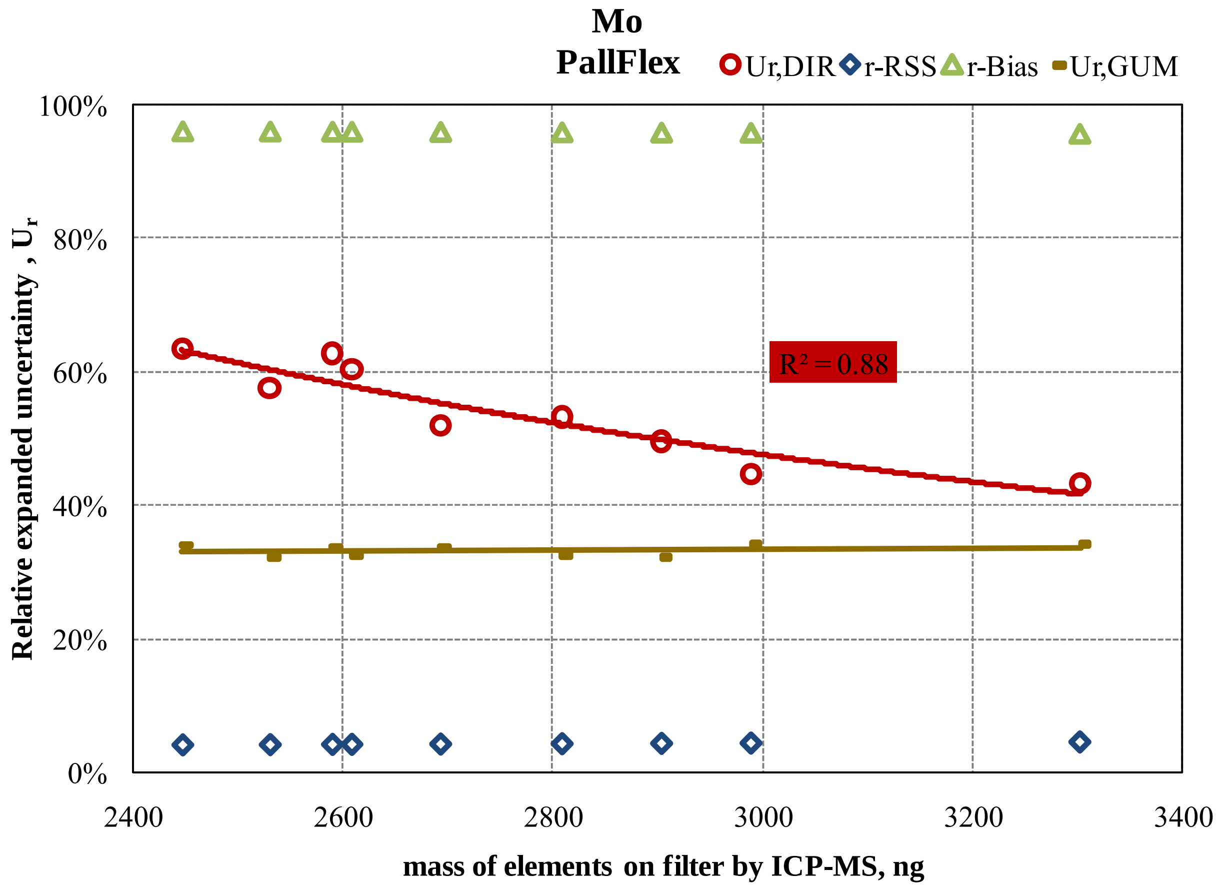


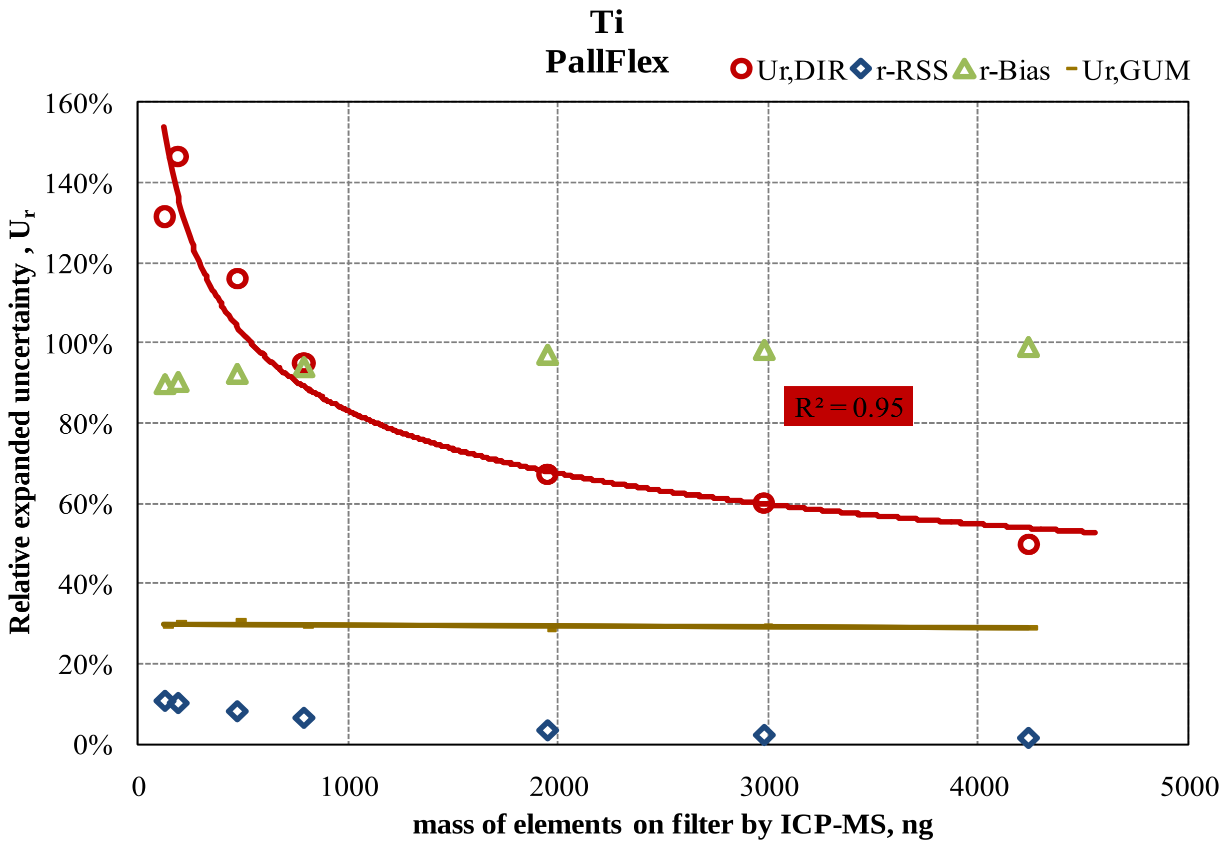
Ni
PallFlex
Ur,DIR
r-RSS
r-Bias
Ur,GUM
m_{limit}
R² = 0.49
Relative expanded uncertainty , U_r
250%
200%
150%
100%
50%
0%
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
mass of elements on filter by ICP-MS, ng


Cr
PallFlex
Ur,DIR
r-RSS
r-Bias
Ur,GUM
Relative expanded uncertainty , U_r
350%
300%
250%
200%
150%
100%
50%
0%
R² = 0.80
200
400
600
800
1000
1200
mass of elements on filter by ICP-MS, ng


Cu
PallFlex
Ur,DIR
r-RSS
r-Bias
Ur,GUM
Relative expanded uncertainty , U_r
300%
250%
200%
150%
100%
50%
0%
R² = 1.00
1000
2000
3000
4000
5000
6000
mass of elements on filter by ICP-MS, ng


Mn
PallFlex
Ur,DIR
r-RSS
r-Bias
Ur,GUM
250%
200%
150%
100%
50%
0%
Relative expanded uncertainty , U_r
R² = 0.93
0
1000
2000
3000
4000
5000
6000
mass of elements on filter by ICP-MS, ng


Mo
PallFlex
Ur,DIR
r-RSS
r-Bias
Ur,GUM
100%
80%
60%
40%
20%
0%
Relative expanded uncertainty , U_r
R² = 0.88
2400
2600
2800
3000
3200
3400
mass of elements on filter by ICP-MS, ng



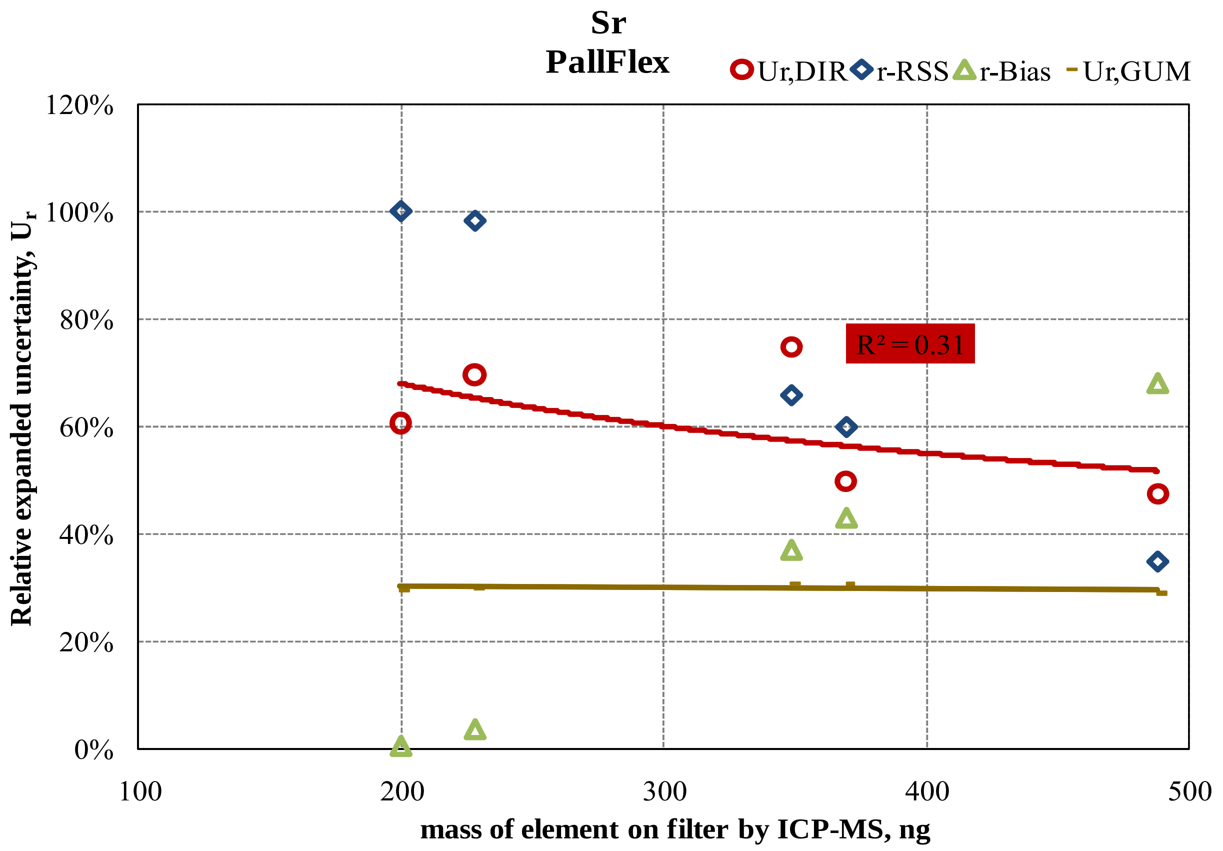
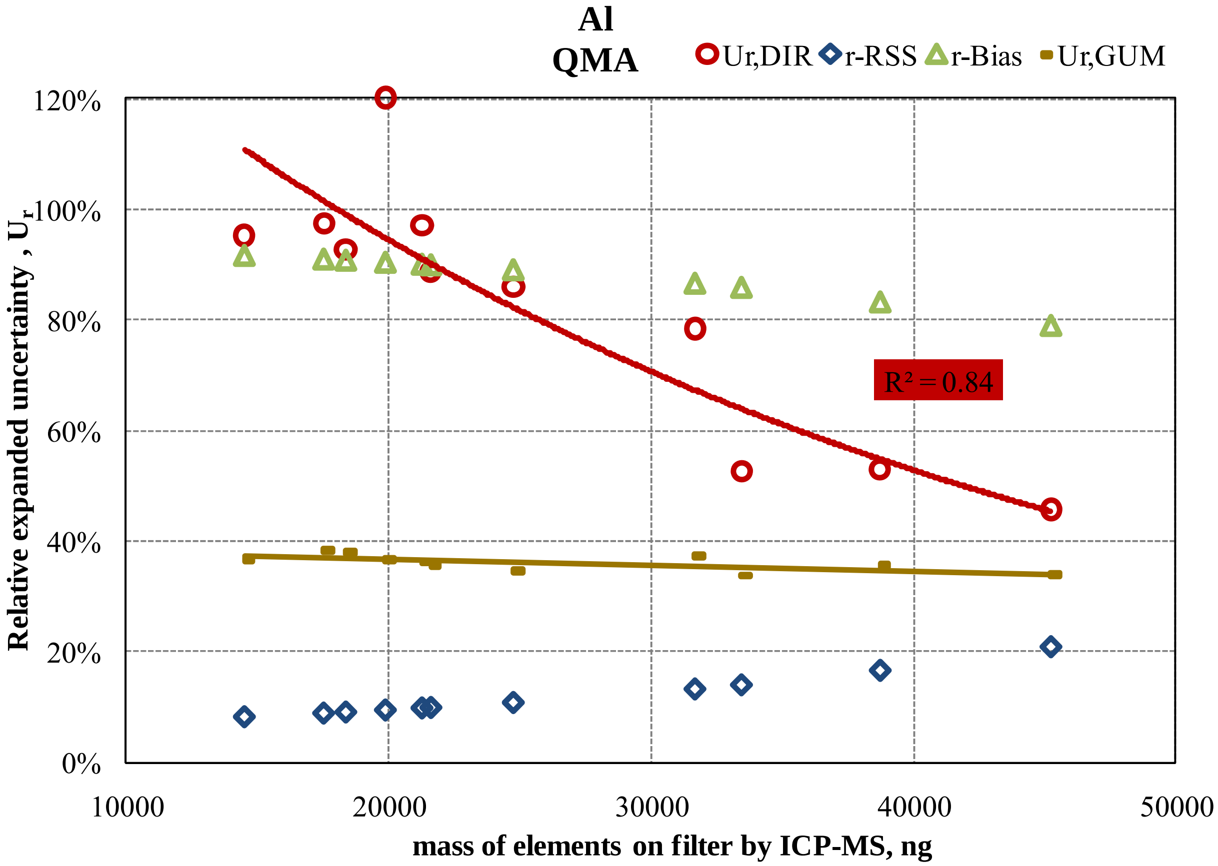
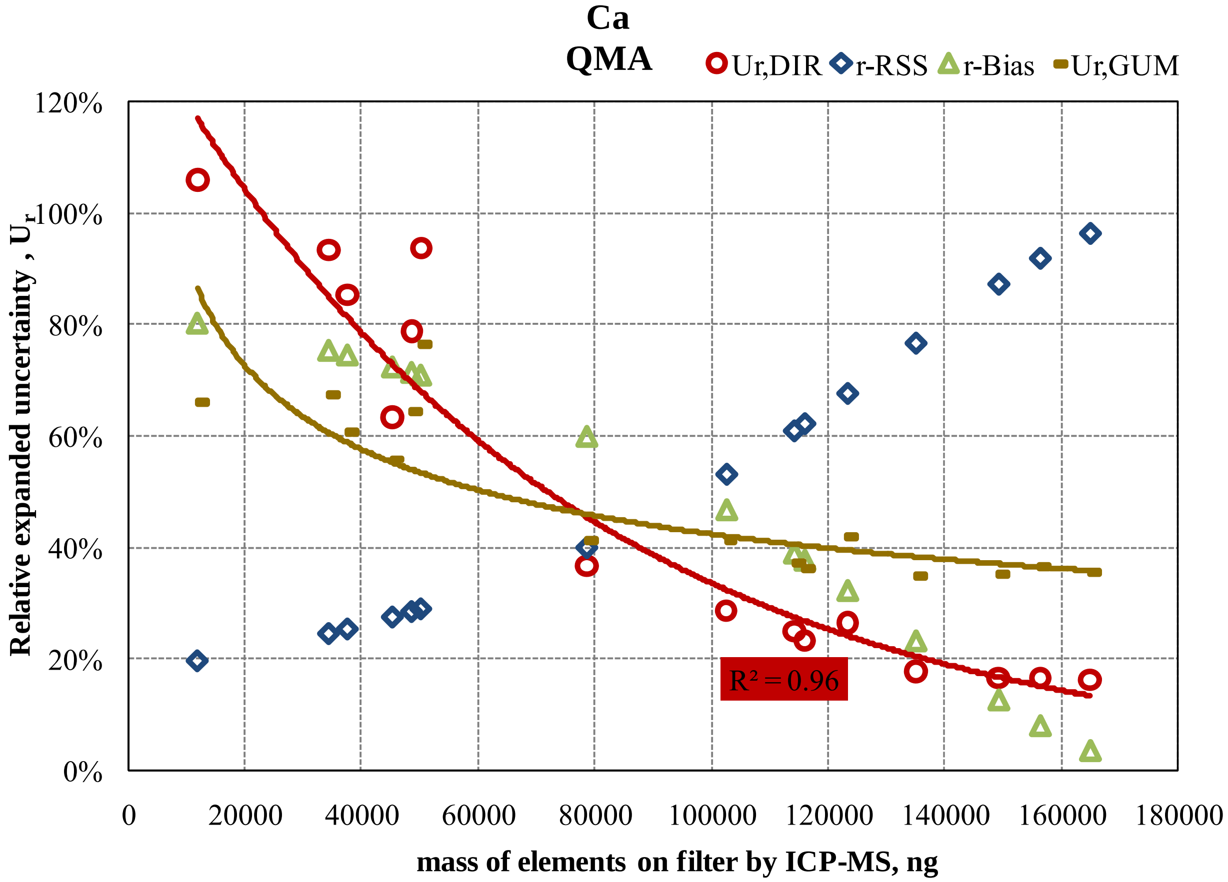
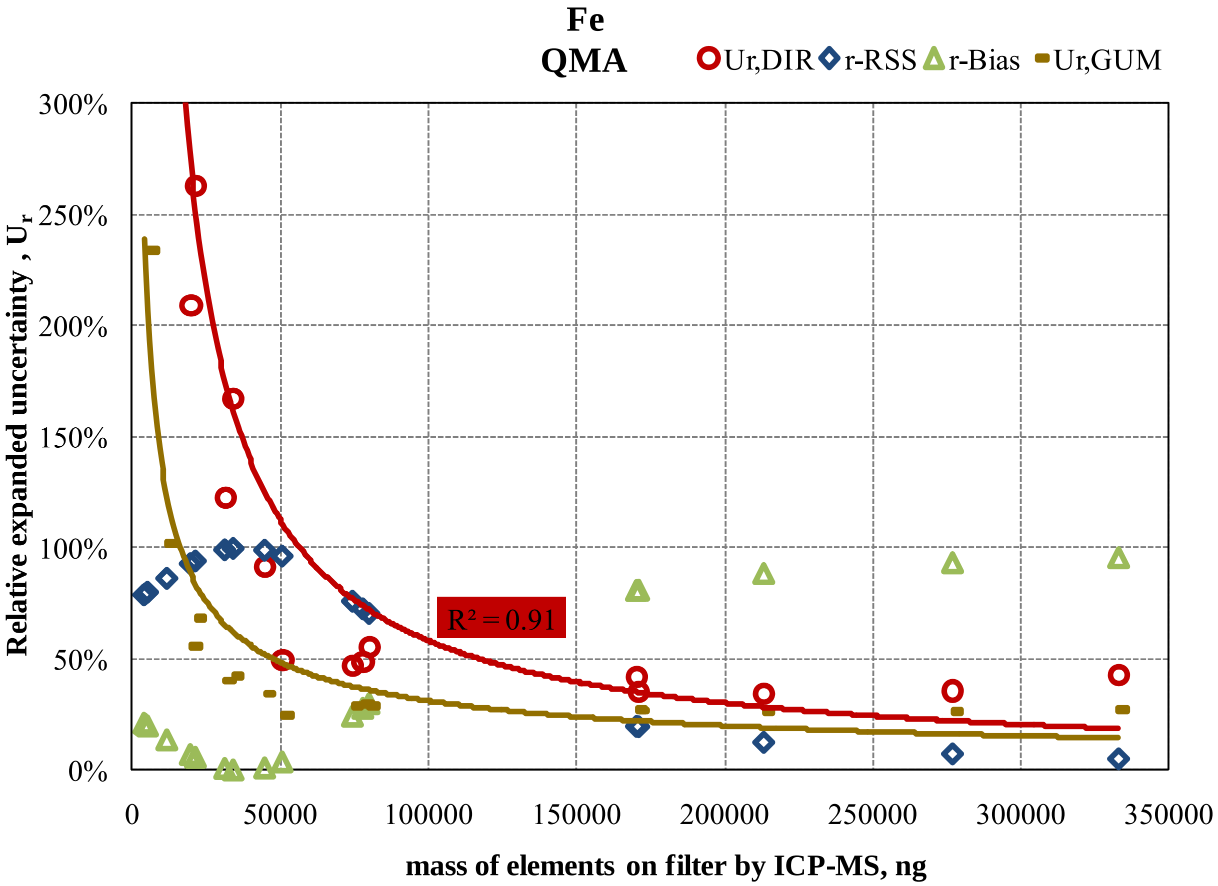
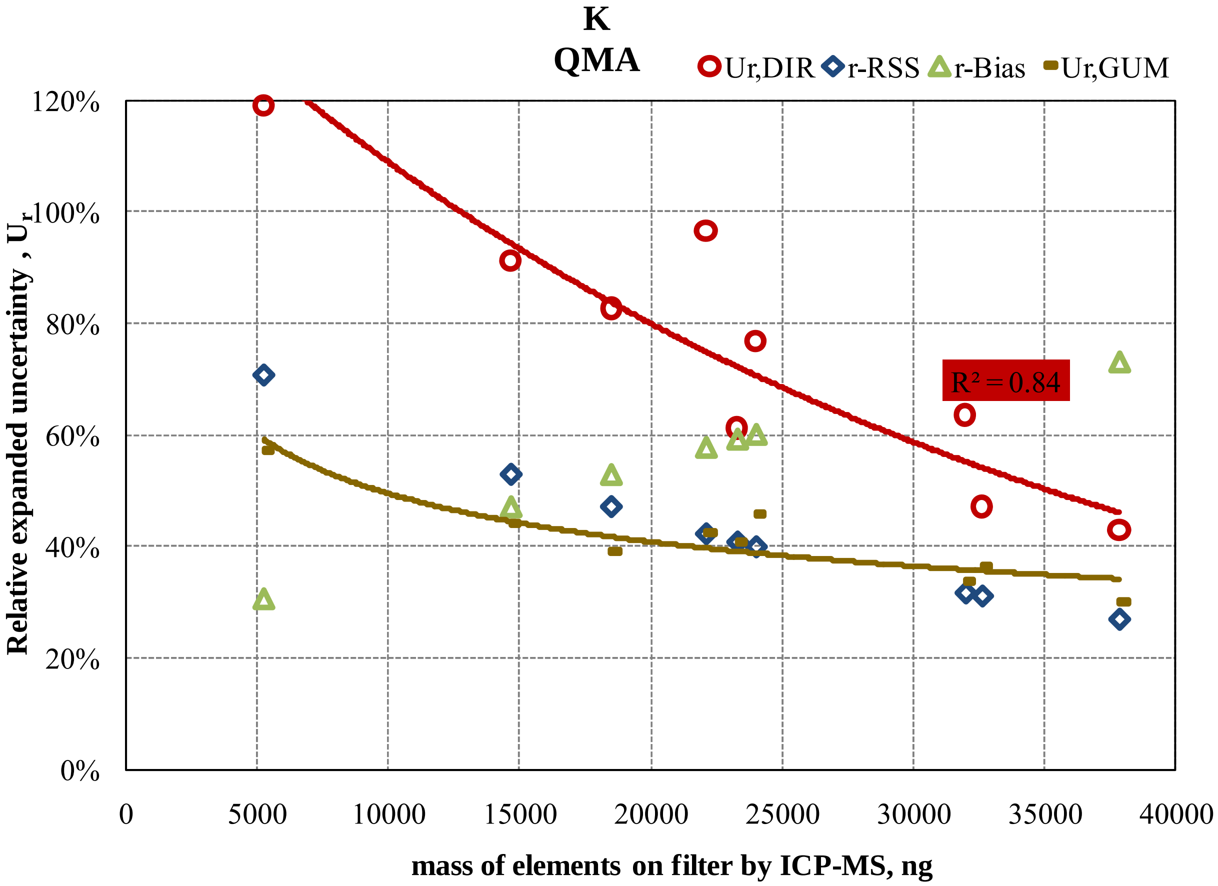


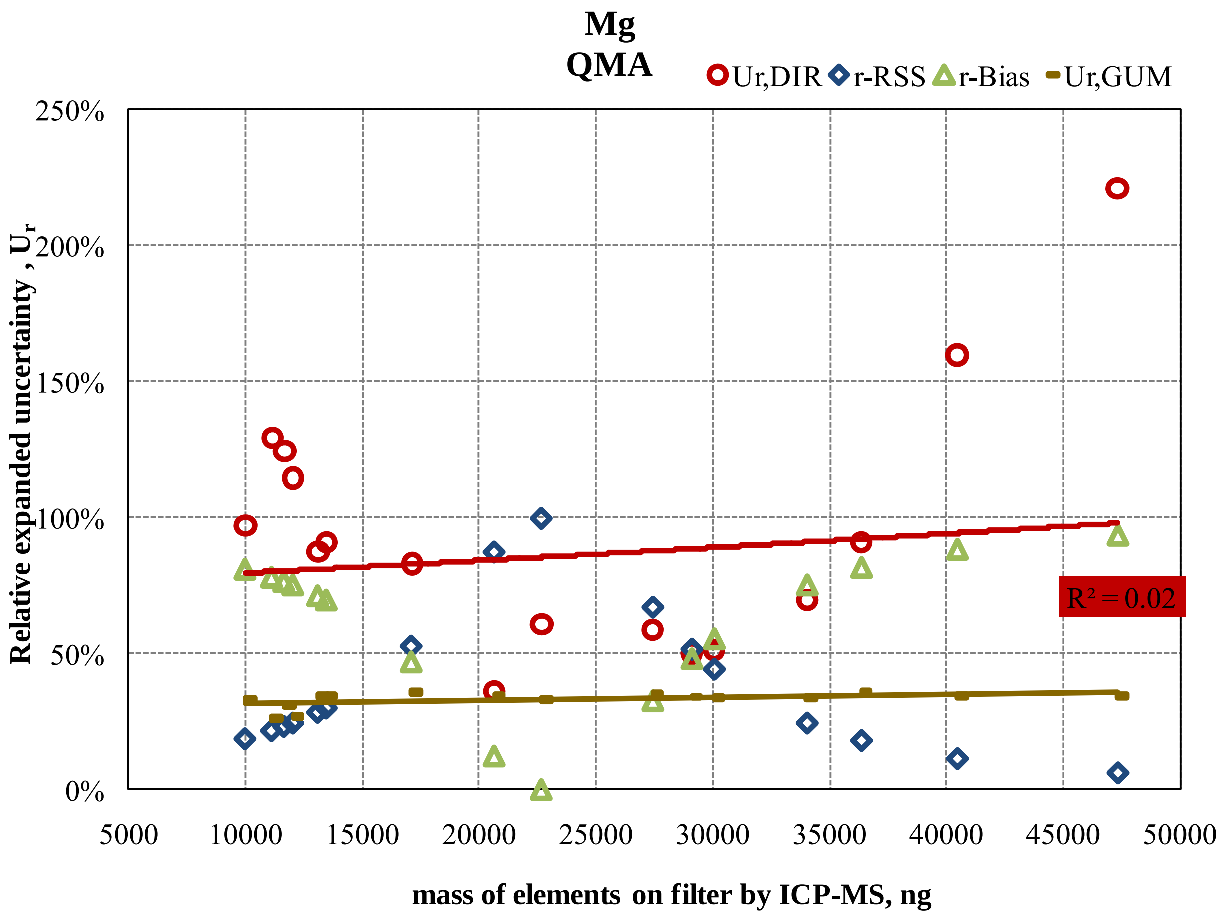
Figure 9: Comparison of $U_{r,GUM}$ and $U_{r,DIR}$ for PallFlex filters. m_{lim} denotes the limit values of EU Directives and calculated by assuming 55 m^3 sampling air

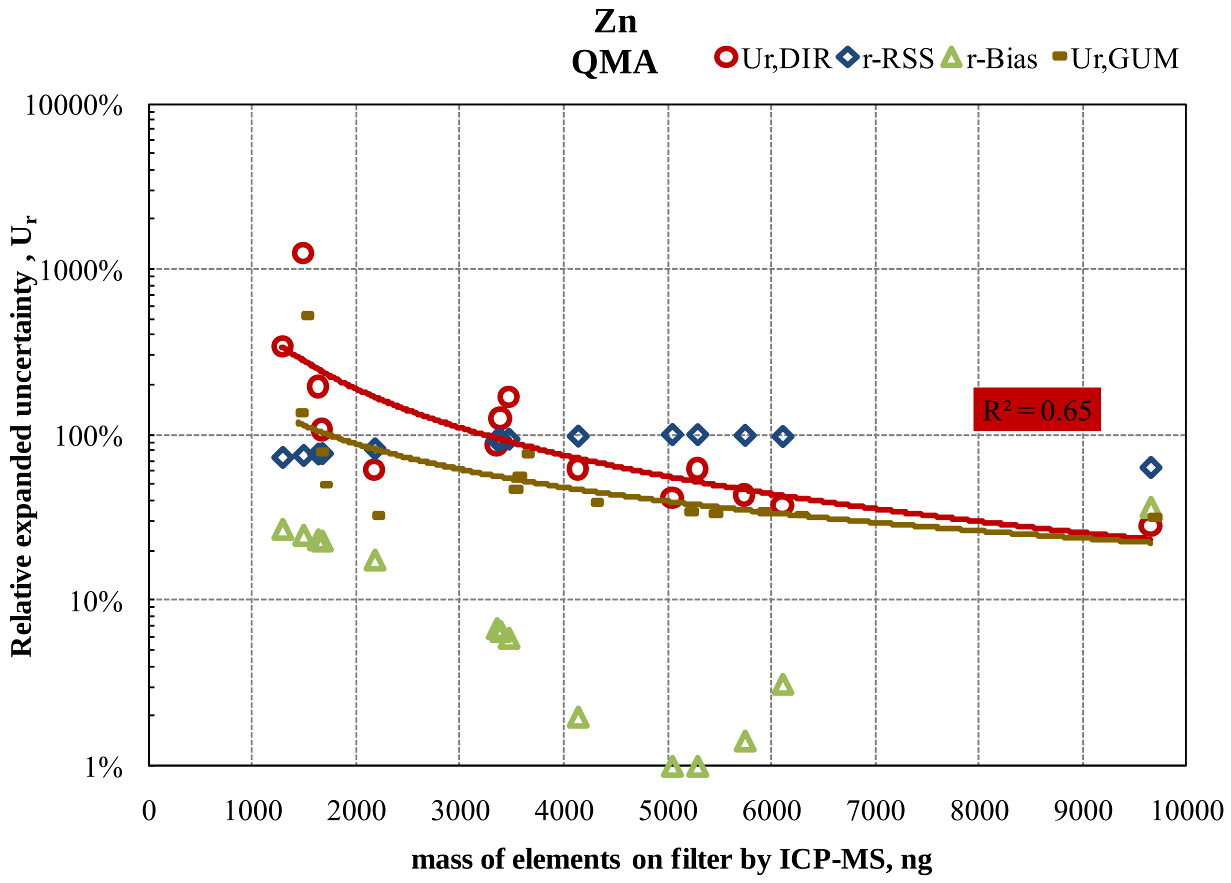

Al
QMA
Ur,DIR
r-RSS
r-Bias
Ur,GUM
120%
100%
80%
60%
40%
20%
0%
Relative expanded uncertainty , U_r
R² = 0.84
10000
20000
30000
40000
50000
mass of elements on filter by ICP-MS, ng

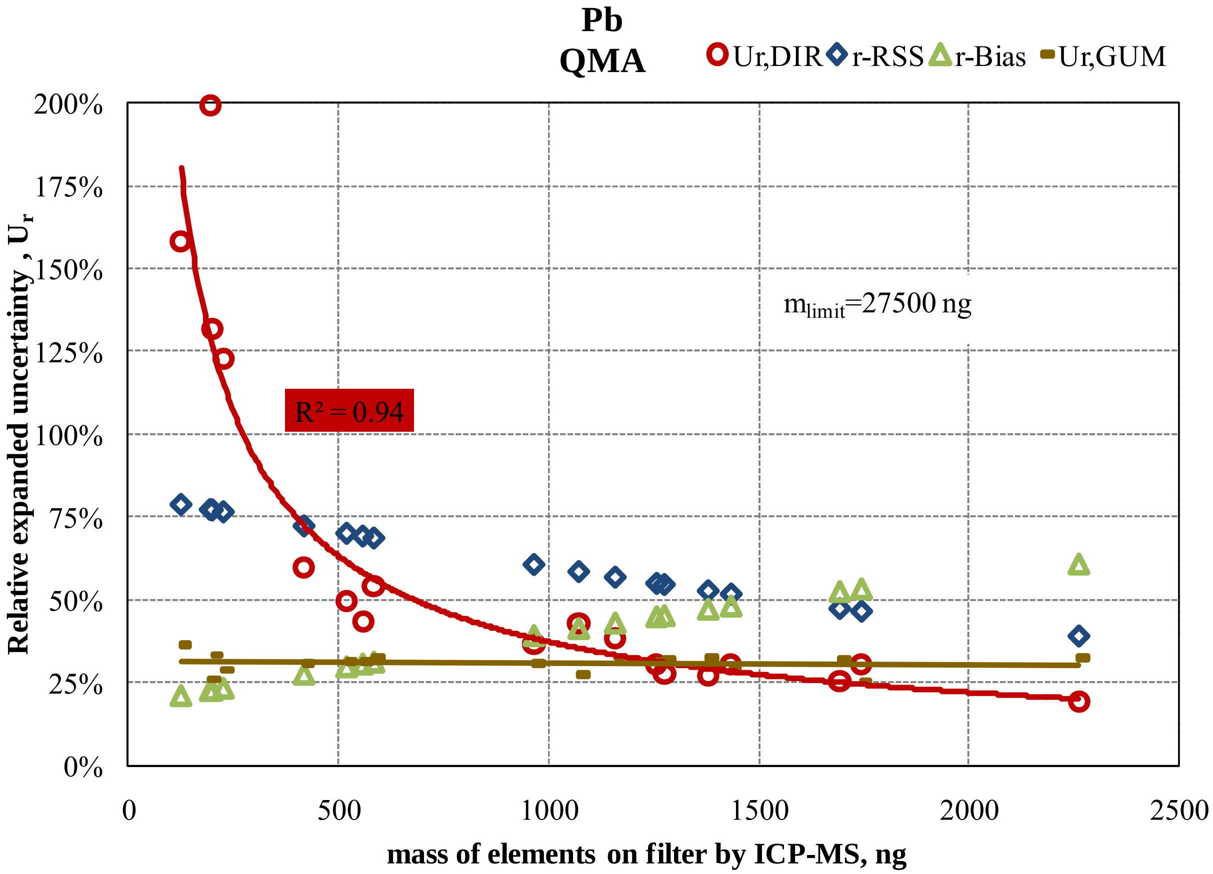

Ca
QMA
Ur,DIR
r-RSS
r-Bias
Ur,GUM
120%
100%
80%
60%
40%
20%
0%
Relative expanded uncertainty , U_r
R² = 0.96
0
20000
40000
60000
80000
100000
120000
140000
160000
180000
mass of elements on filter by ICP-MS, ng

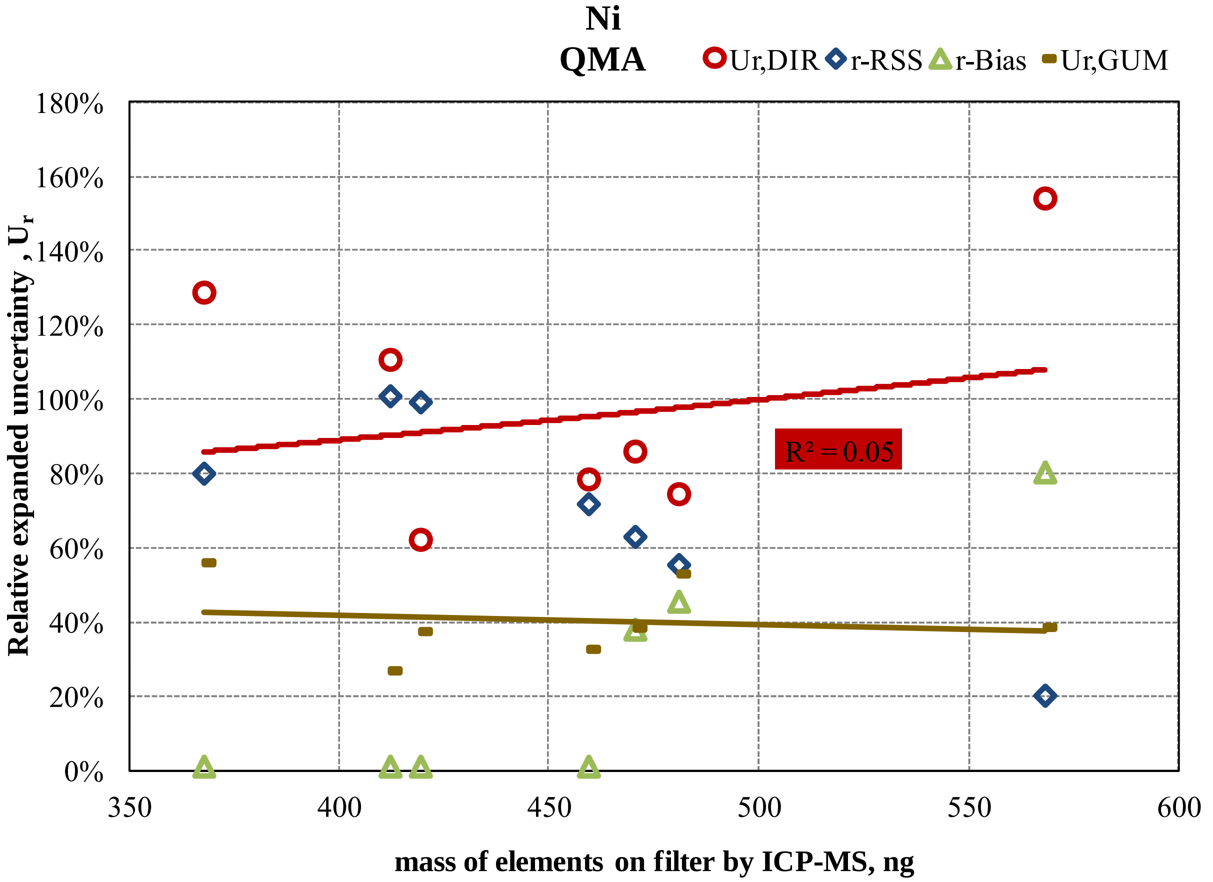

Fe
QMA
Ur,DIR
r-RSS
r-Bias
Ur,GUM
300%
250%
200%
150%
100%
50%
0%
Relative expanded uncertainty , U$_r$
R² = 0.91
0
50000
100000
150000
200000
250000
300000
350000
mass of elements on filter by ICP-MS, ng

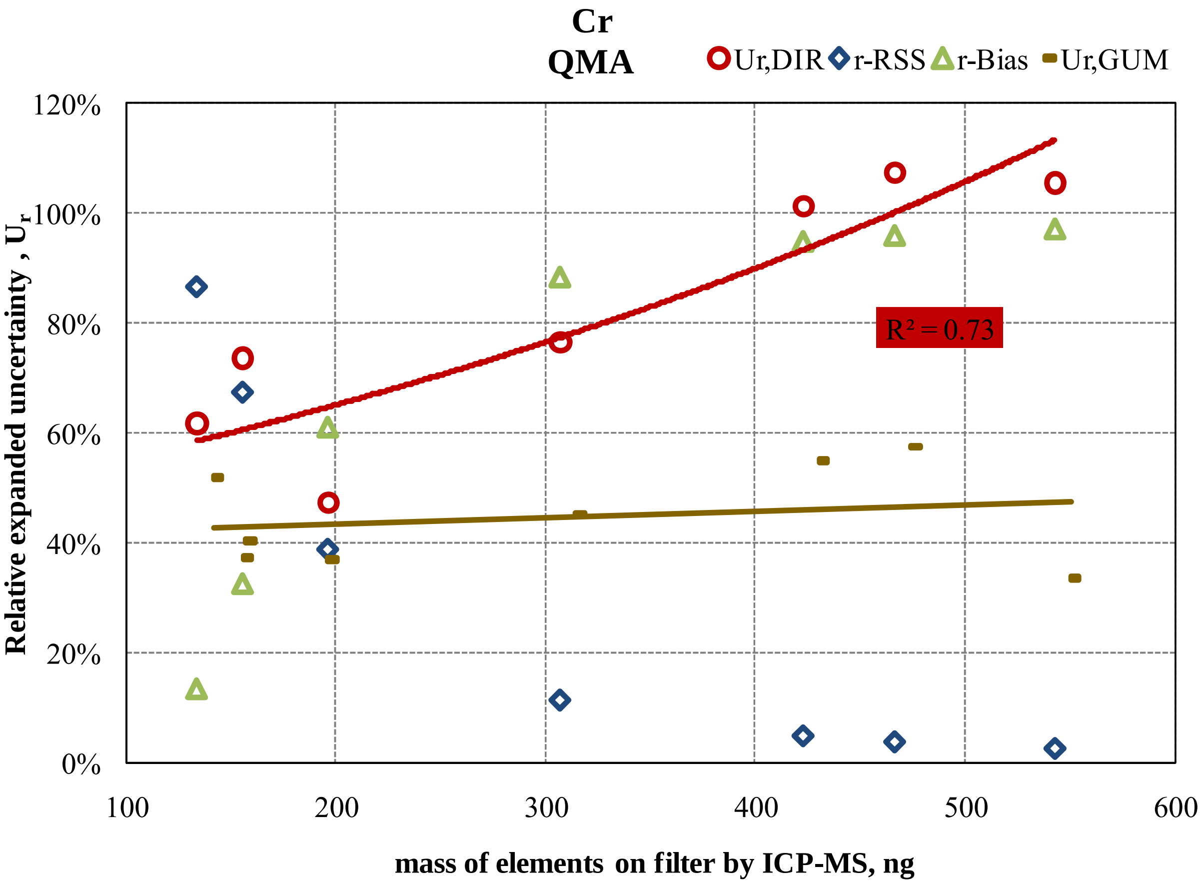

K
QMA
Ur,DIR
r-RSS
r-Bias
Ur,GUM
120%
100%
80%
60%
40%
20%
0%
Relative expanded uncertainty , U$_r$
R² = 0.84
0
5000
10000
15000
20000
25000
30000
35000
40000
mass of elements on filter by ICP-MS, ng

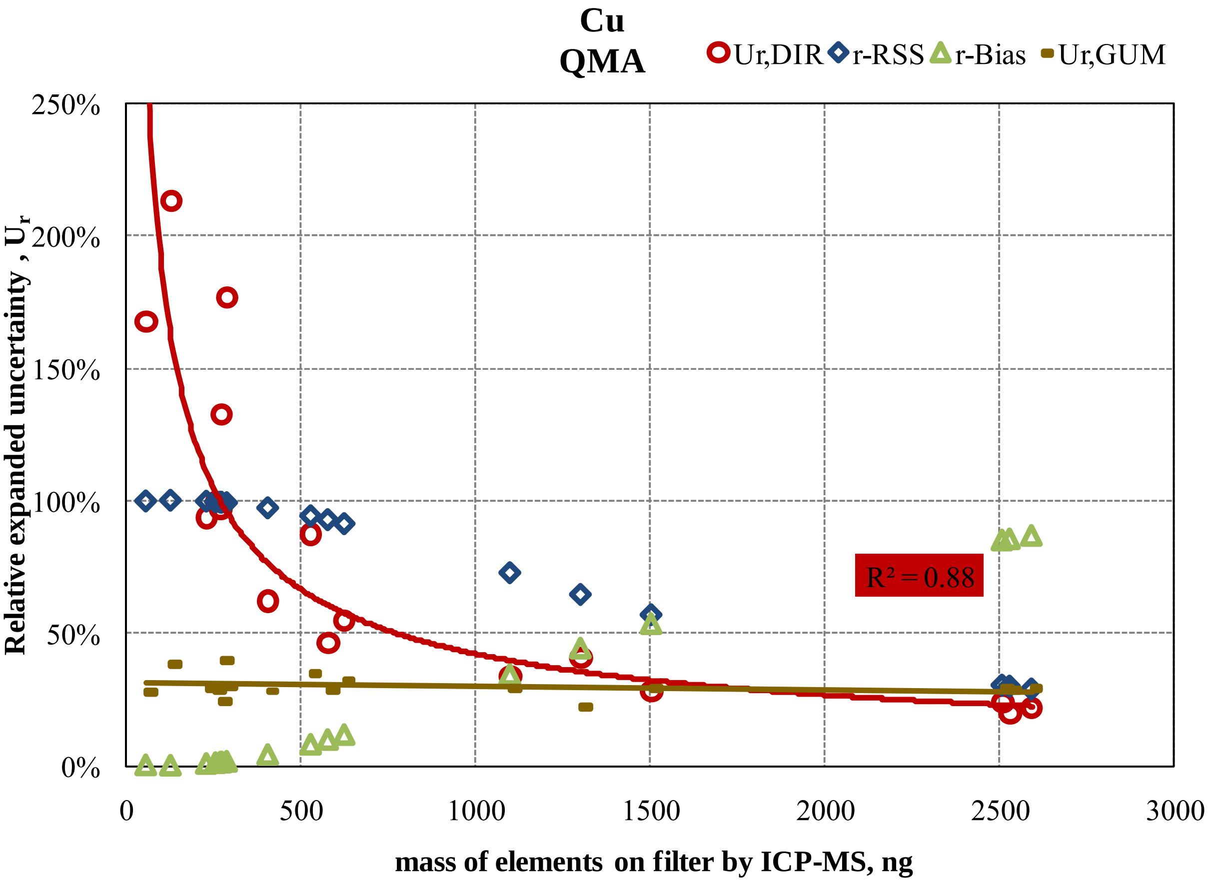

Mg
QMA
Ur,DIR
r-RSS
r-Bias
Ur,GUM
250%
200%
150%
100%
50%
0%
Relative expanded uncertainty , U_r
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
mass of elements on filter by ICP-MS, ng
R² = 0.02


Zn
QMA
Ur,DIR
r-RSS
r-Bias
Ur,GUM
10000%
1000%
100%
10%
1%
Relative expanded uncertainty , U_r
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
mass of elements on filter by ICP-MS, ng
R² = 0.65


Pb
QMA
Ur,DIR
r-RSS
r-Bias
Ur,GUM
Relative expanded uncertainty , U$_r$
200%
175%
150%
125%
100%
75%
50%
25%
0%
0
500
1000
1500
2000
2500
mass of elements on filter by ICP-MS, ng
m$_{limit}$=27500 ng
R² = 0.94


Ni
QMA
Ur,DIR
r-RSS
r-Bias
Ur,GUM
Relative expanded uncertainty , U$_r$
180%
160%
140%
120%
100%
80%
60%
40%
20%
0%
350
400
450
500
550
600
mass of elements on filter by ICP-MS, ng
R² = 0.05


Cr
QMA
Ur,DIR
r-RSS
r-Bias
Ur,GUM
120%
100%
80%
60%
40%
20%
0%
Relative expanded uncertainty , U_r
R² = 0.73
100
200
300
400
500
600
mass of elements on filter by ICP-MS, ng


Cu
QMA
Ur,DIR
r-RSS
r-Bias
Ur,GUM
250%
200%
150%
100%
50%
0%
Relative expanded uncertainty , U_r
R² = 0.88
0
500
1000
1500
2000
2500
3000
mass of elements on filter by ICP-MS, ng

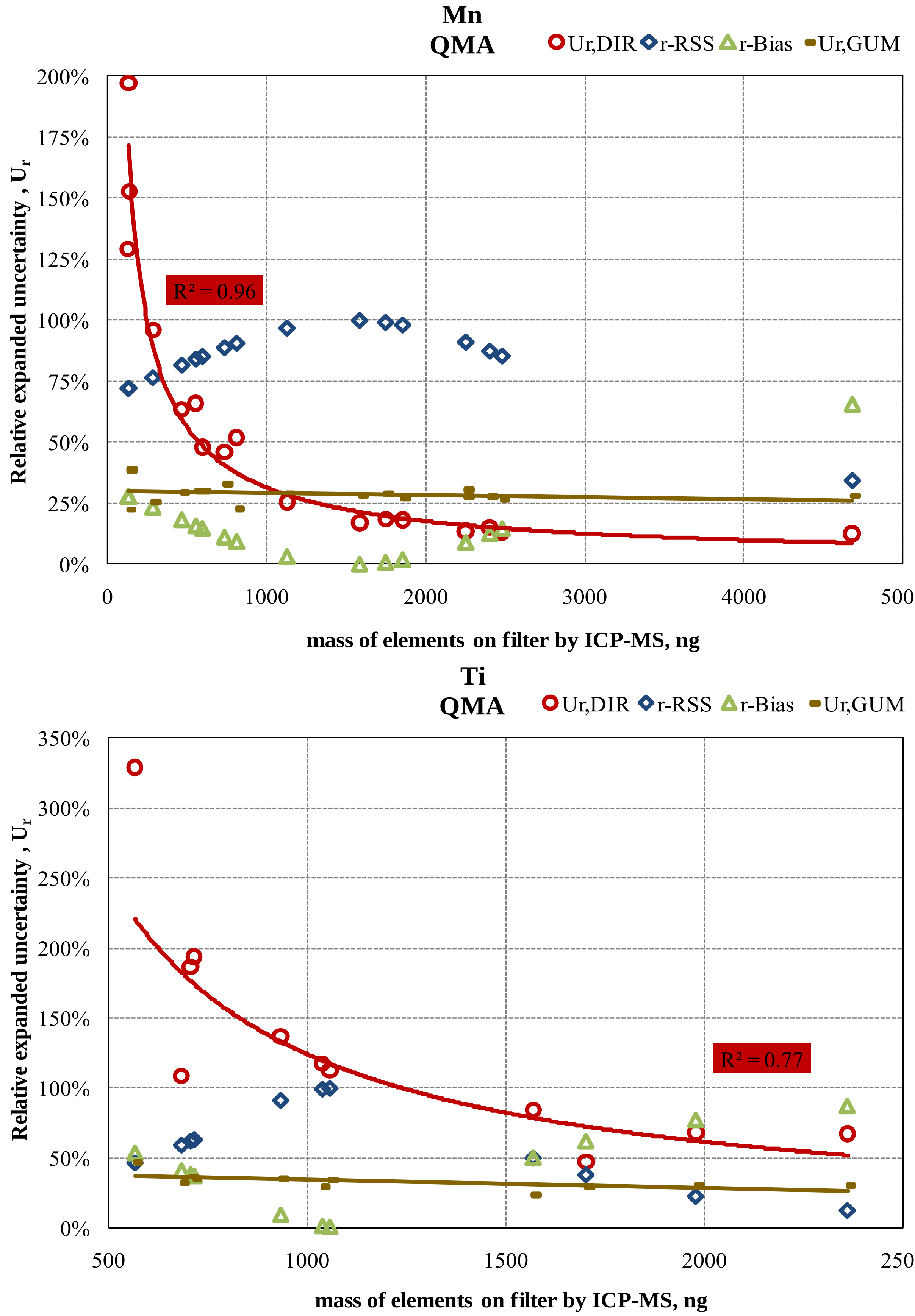
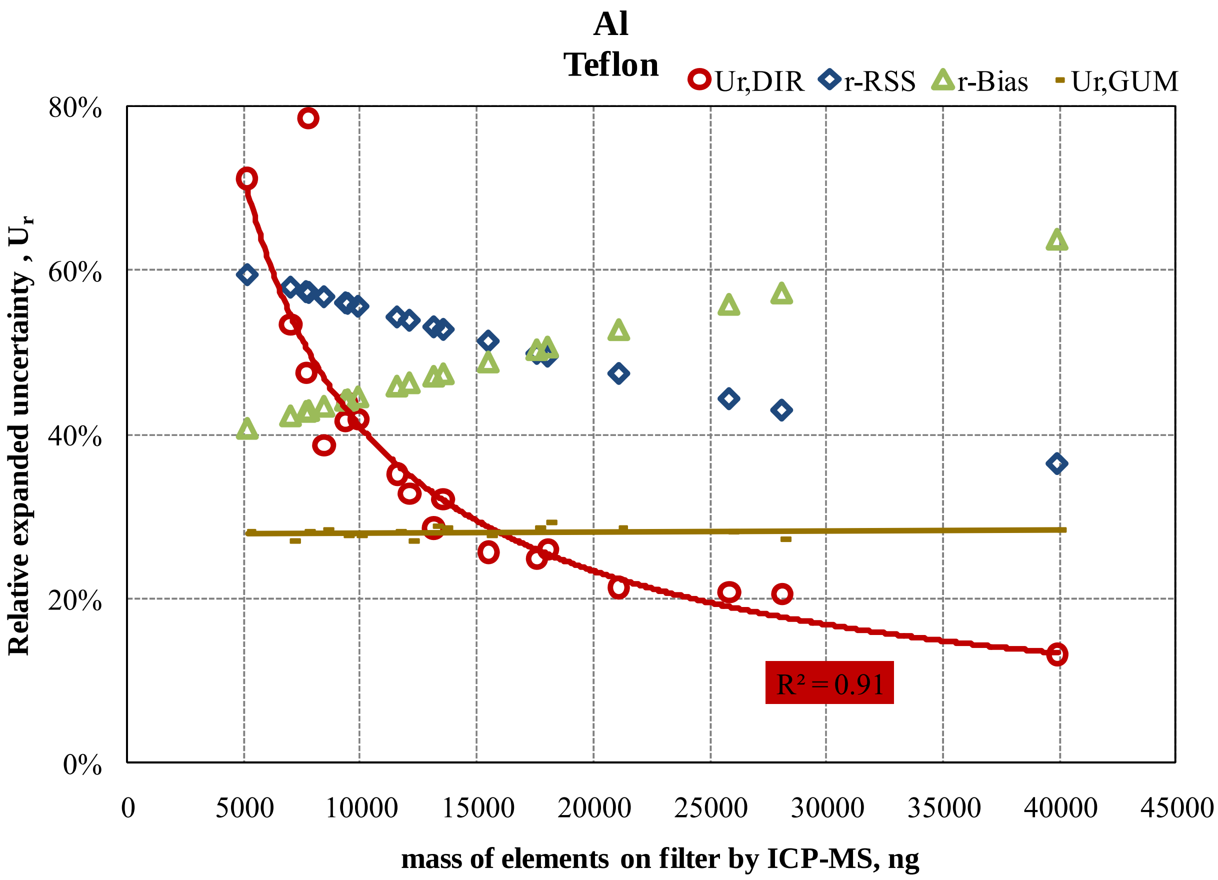
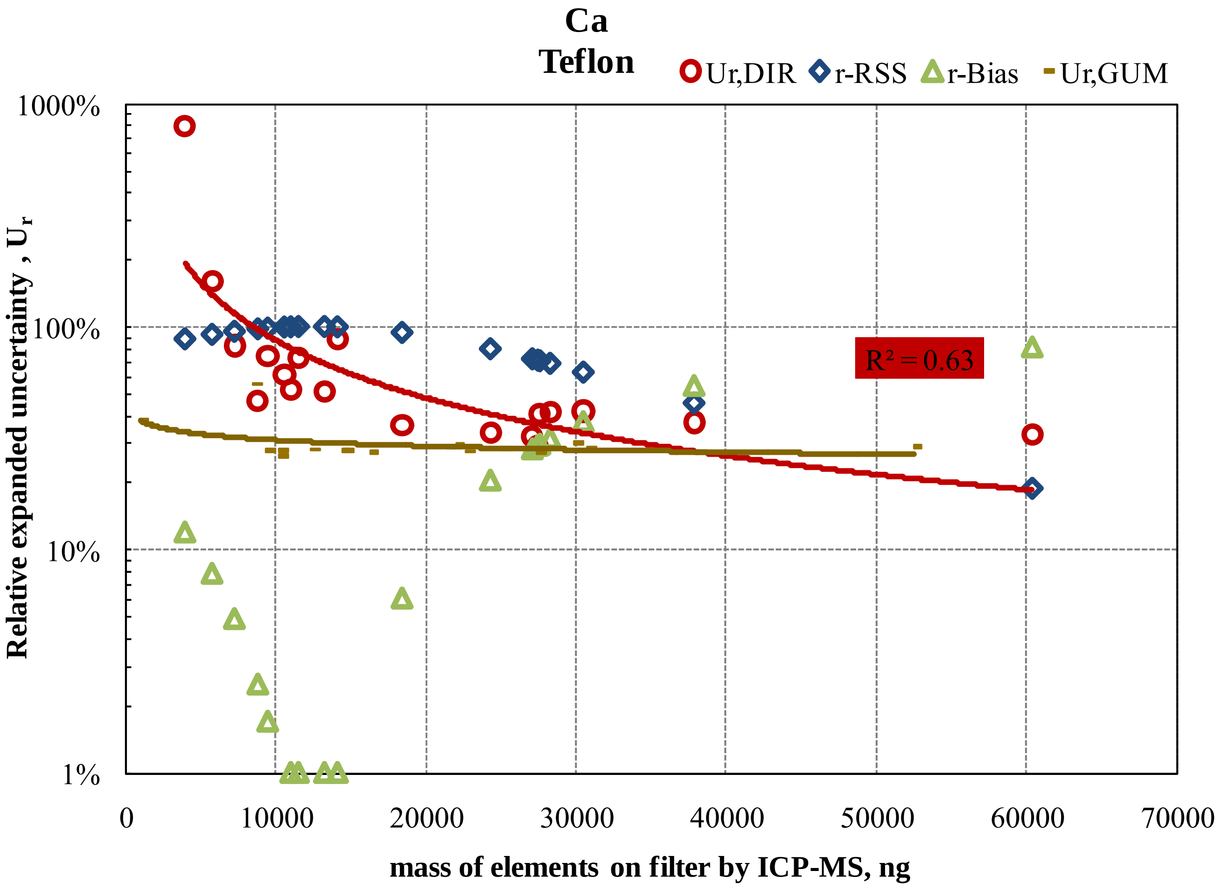
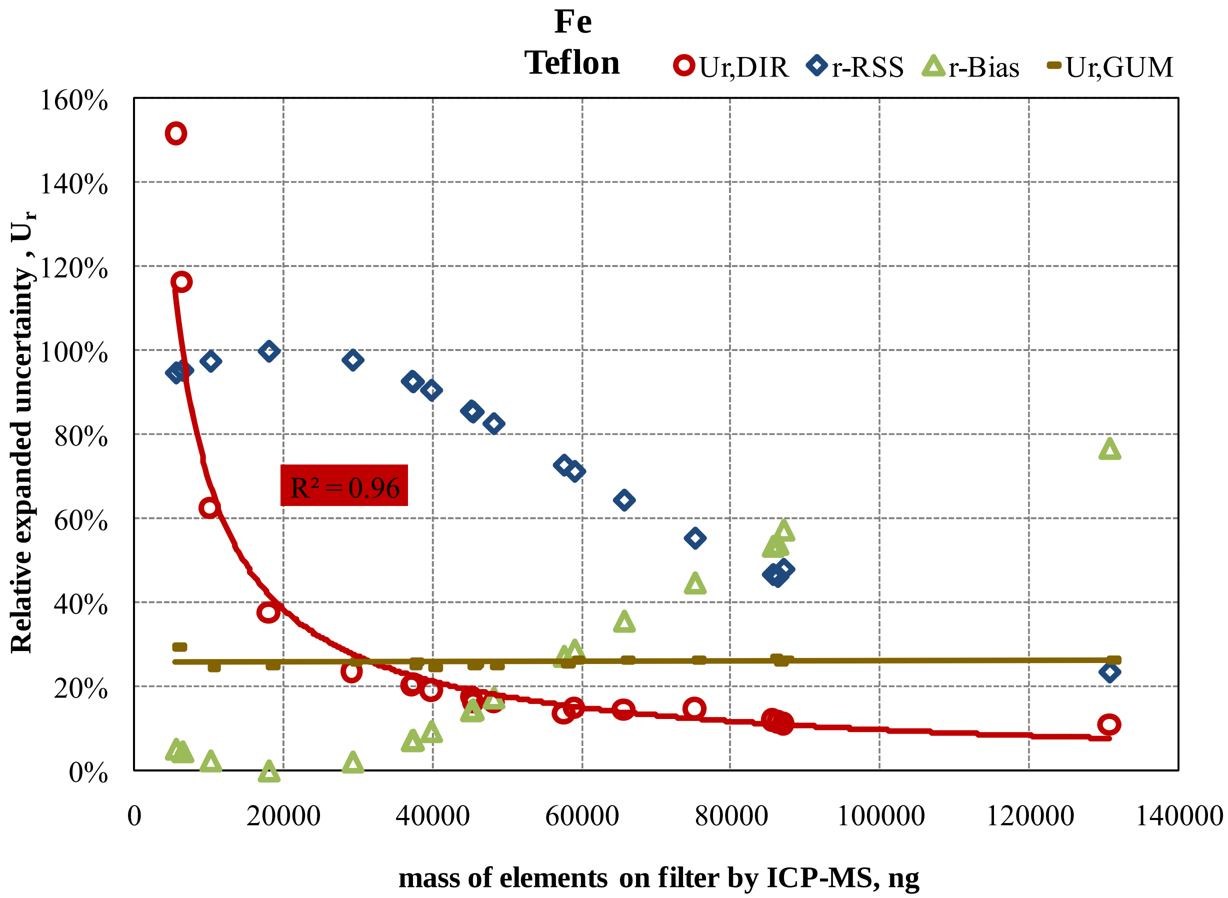
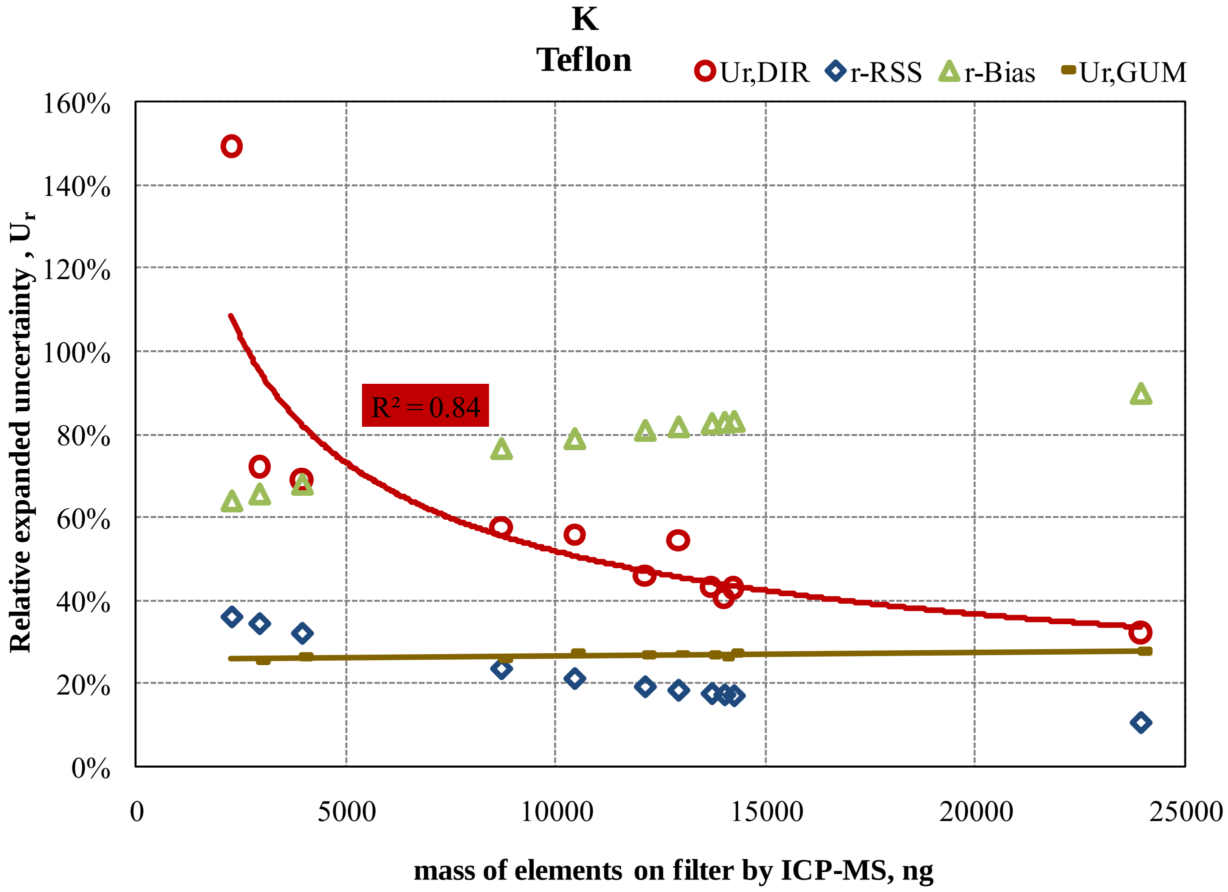


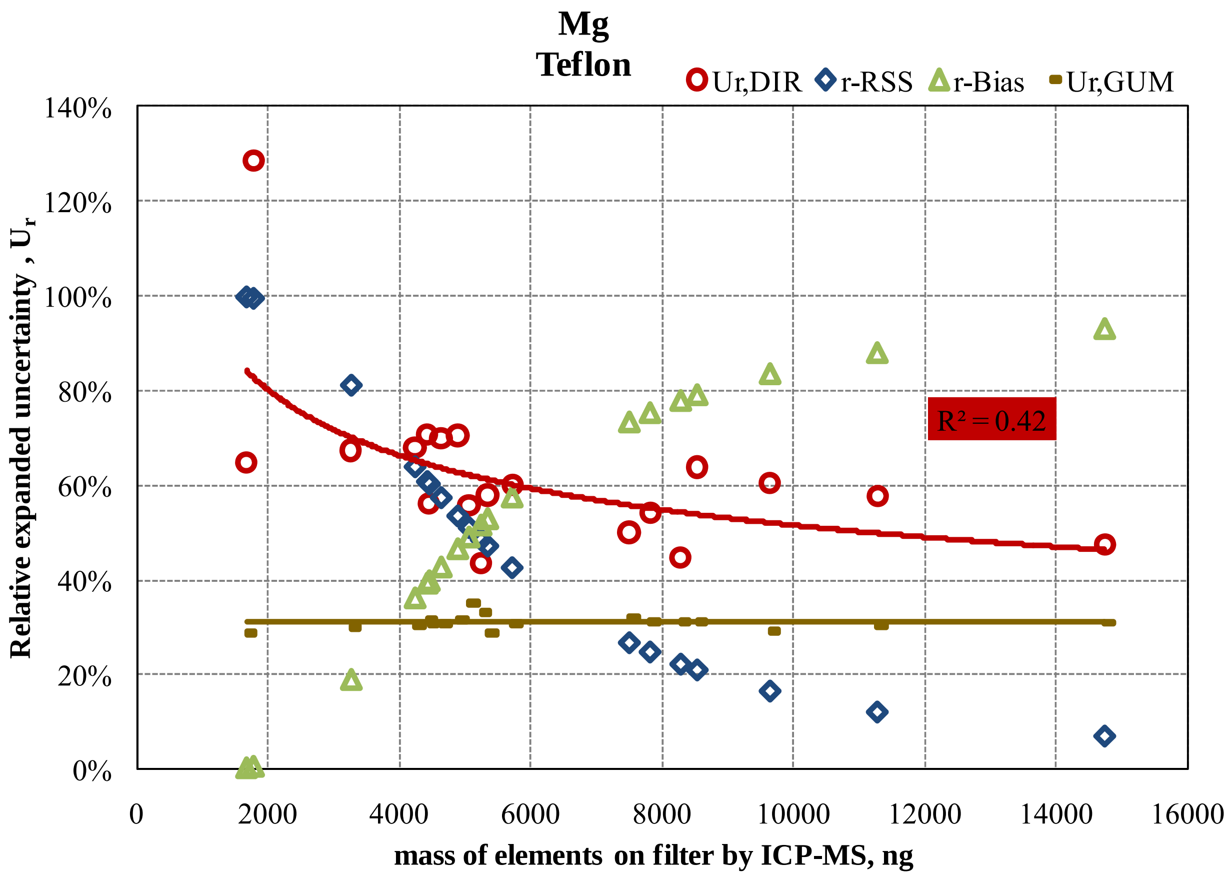
Figure 10: Comparison of $U_{r,GUM}$ and $U_{r,DIR}$ for QMA filters. m_{lim} denotes the limit values of EU Directives and calculated by assuming 55 m^3 sampling air

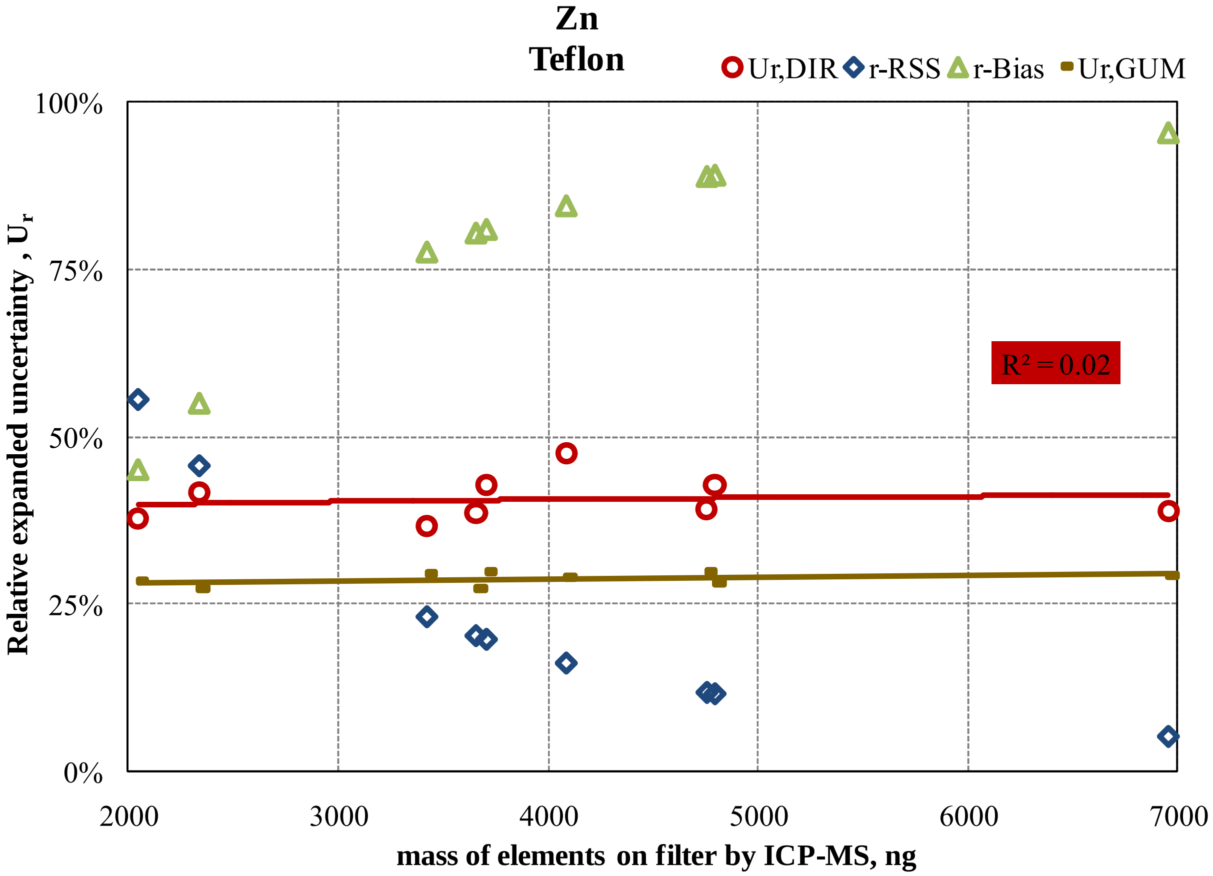

Al
Teflon
Ur,DIR
r-RSS
r-Bias
Ur,GUM
80%
60%
40%
20%
0%
Relative expanded uncertainty , U_r
R² = 0.91
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
mass of elements on filter by ICP-MS, ng

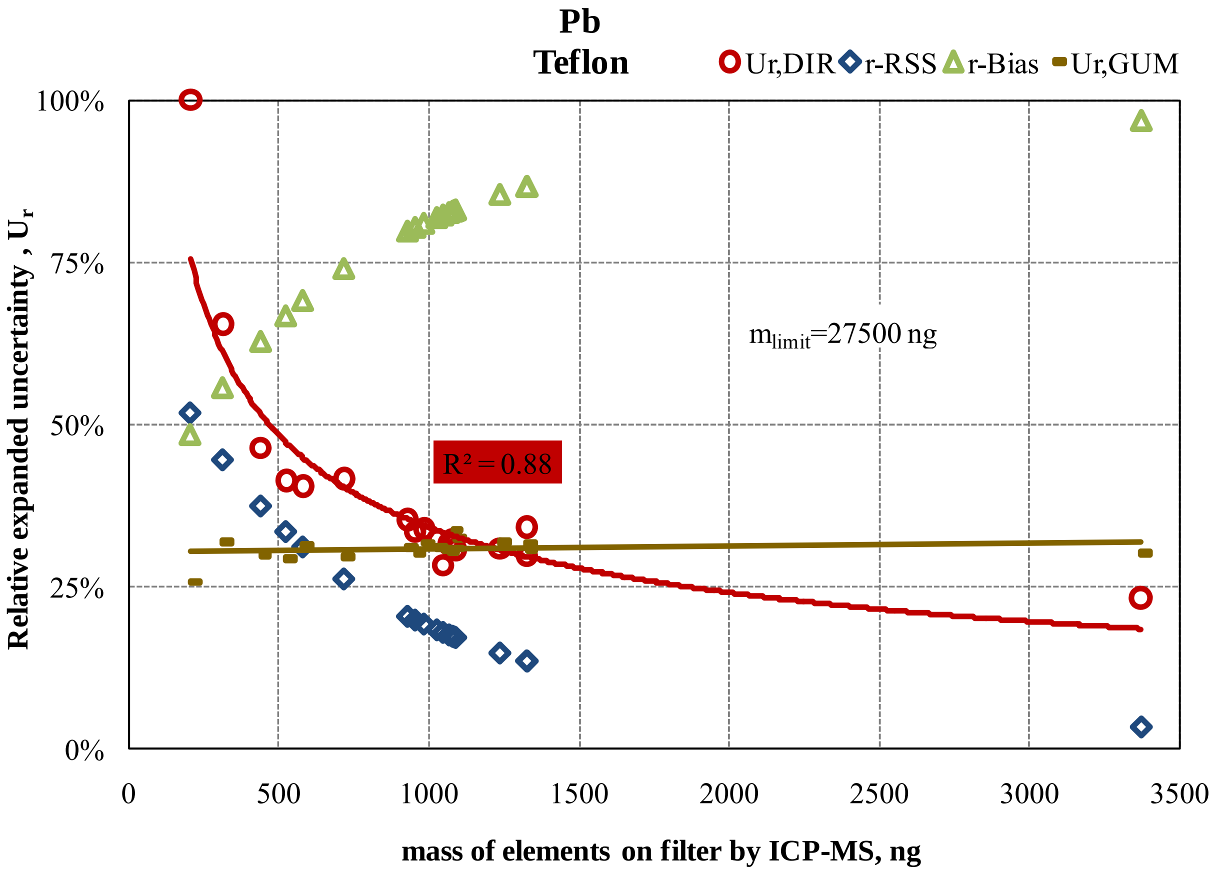

Ca
Teflon
Ur,DIR
r-RSS
r-Bias
Ur,GUM
1000%
100%
10%
1%
Relative expanded uncertainty , U_r
R² = 0.63
0
10000
20000
30000
40000
50000
60000
70000
mass of elements on filter by ICP-MS, ng

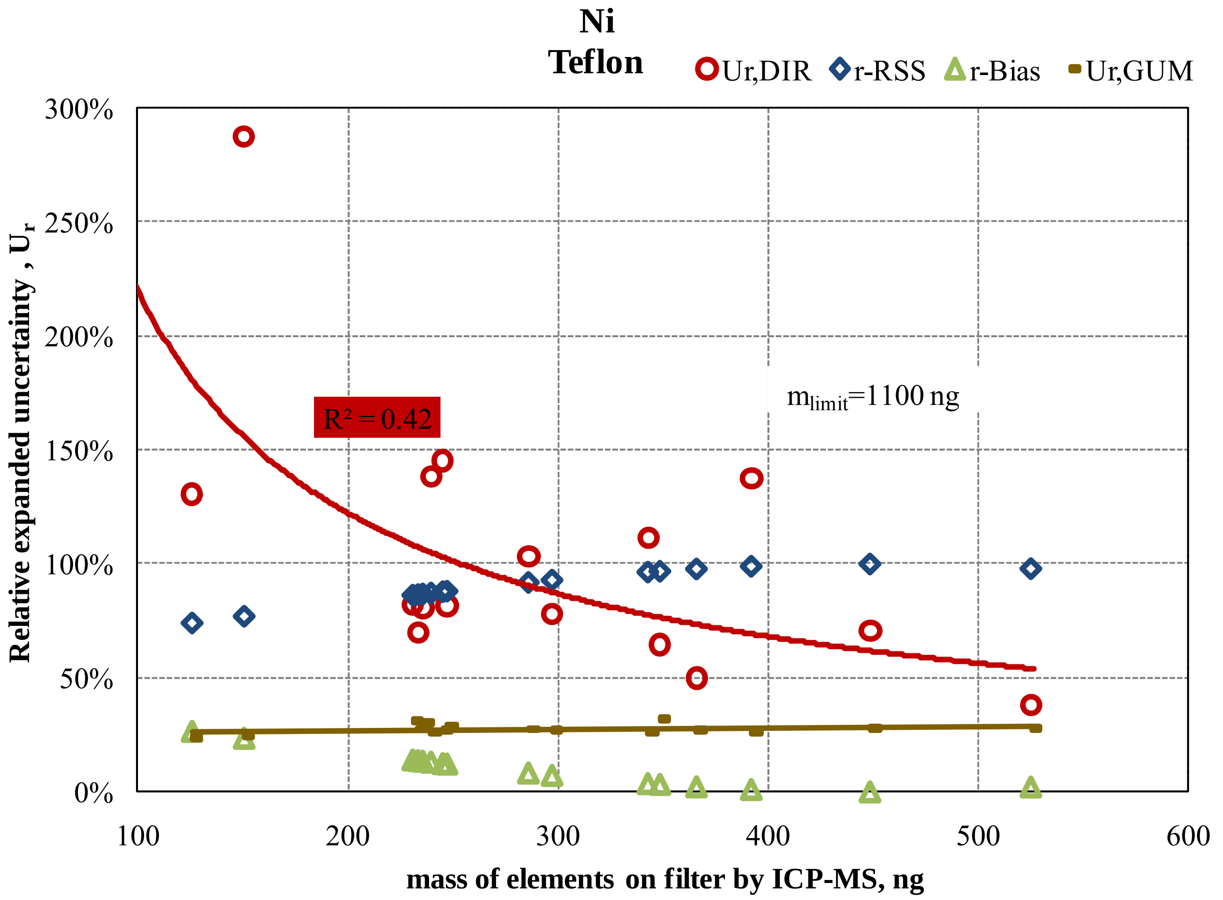

Fe
Teflon
Ur,DIR
r-RSS
r-Bias
Ur,GUM
R² = 0.96
Relative expanded uncertainty , U_r
0%
20%
40%
60%
80%
100%
120%
140%
160%
0
20000
40000
60000
80000
100000
120000
140000
mass of elements on filter by ICP-MS, ng

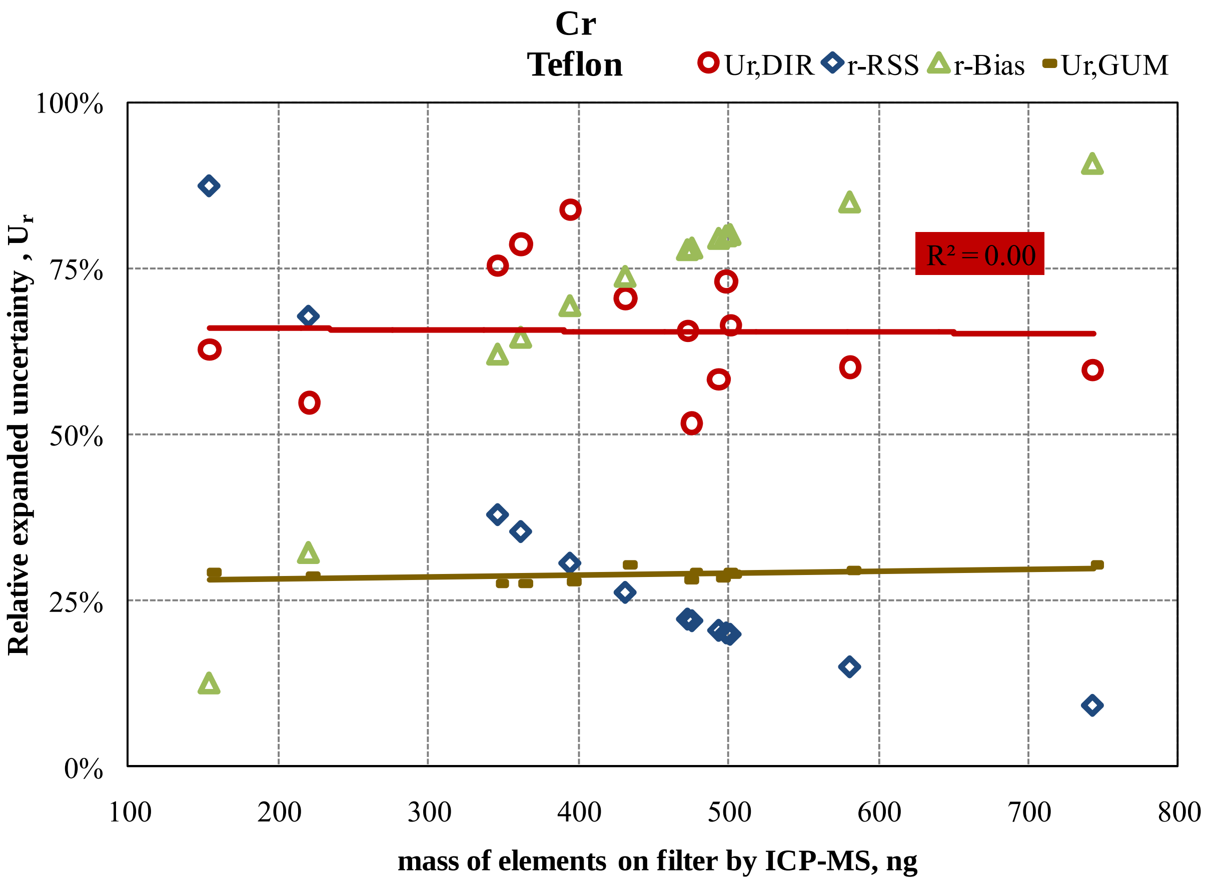

K
Teflon
Ur,DIR
r-RSS
r-Bias
Ur,GUM
R² = 0.84
Relative expanded uncertainty , U_r
0%
20%
40%
60%
80%
100%
120%
140%
160%
0
5000
10000
15000
20000
25000
mass of elements on filter by ICP-MS, ng

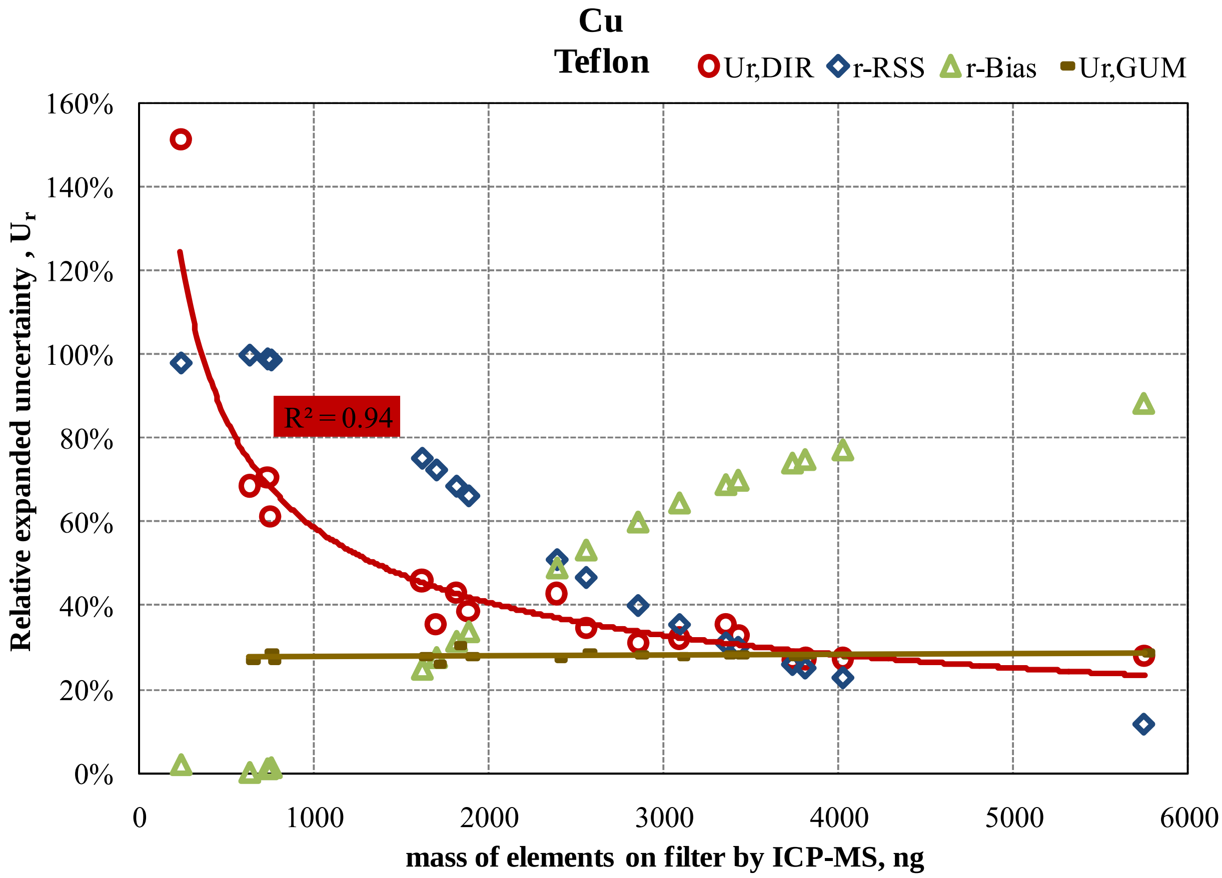

Mg
Teflon
Ur,DIR
r-RSS
r-Bias
Ur,GUM
R² = 0.42
Relative expanded uncertainty , U_r
140%
120%
100%
80%
60%
40%
20%
0%
0
2000
4000
6000
8000
10000
12000
14000
16000
mass of elements on filter by ICP-MS, ng

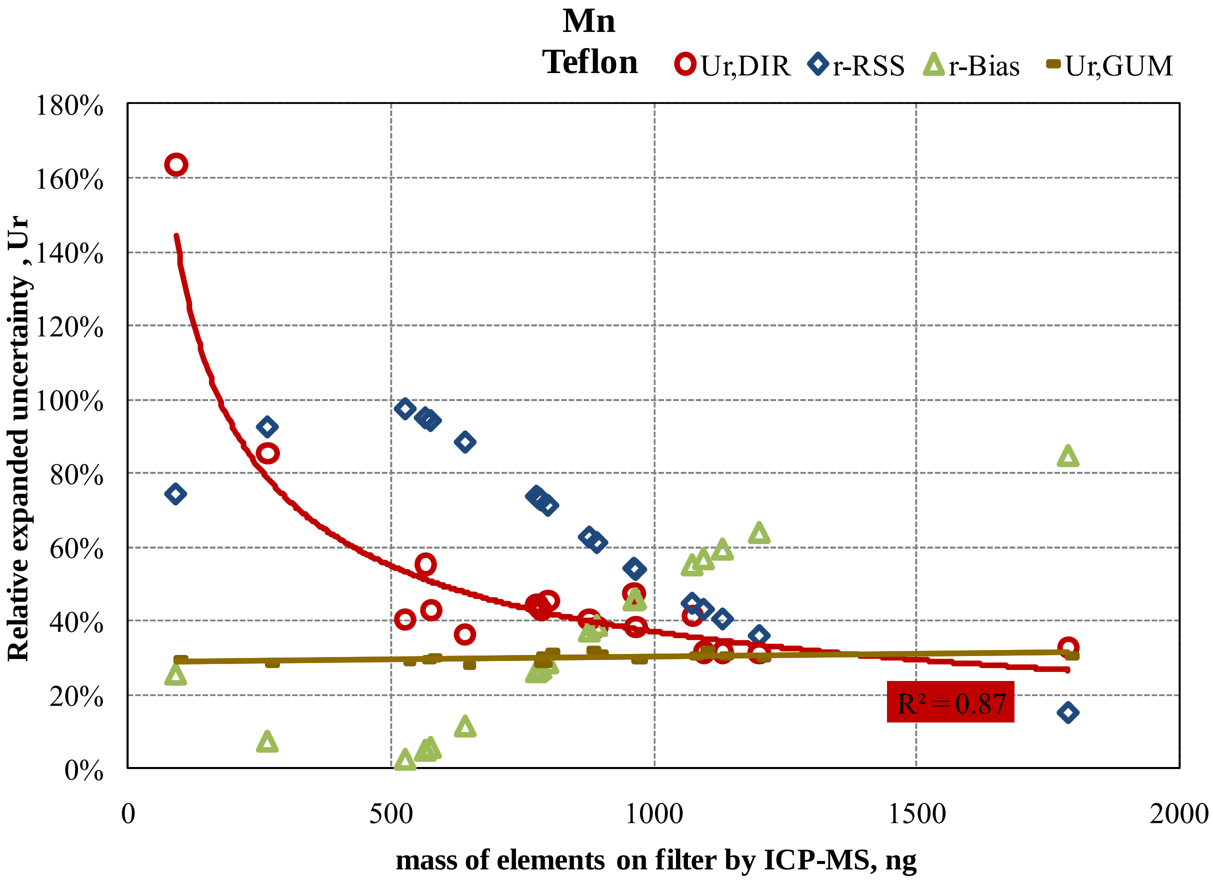

Zn
Teflon
Ur,DIR
r-RSS
r-Bias
Ur,GUM
R² = 0.02
Relative expanded uncertainty , U_r
100%
75%
50%
25%
0%
2000
3000
4000
5000
6000
7000
mass of elements on filter by ICP-MS, ng

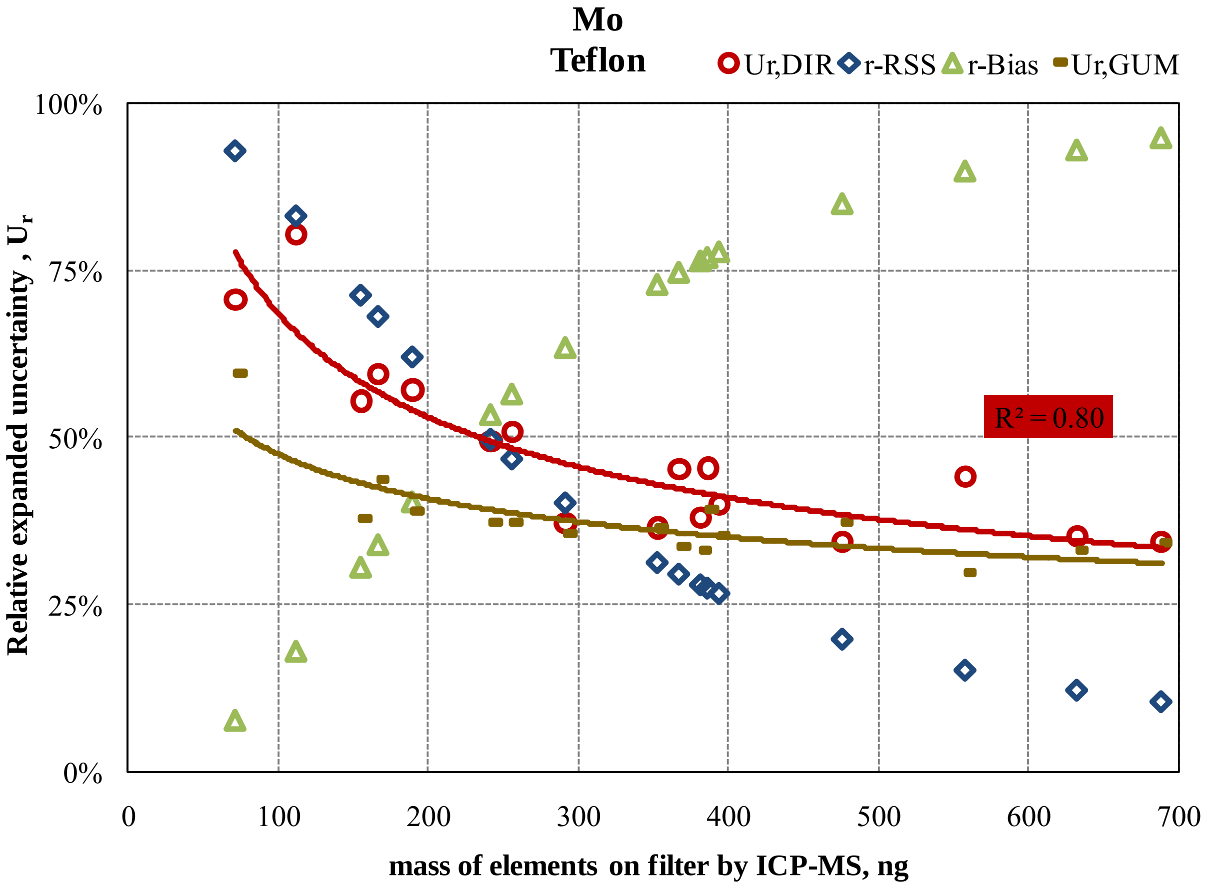

Pb
Teflon
Ur,DIR
r-RSS
r-Bias
Ur,GUM
100%
75%
50%
25%
0%
Relative expanded uncertainty , U_r
m_{limit}=27500 ng
$R^2 = 0.88$
0
500
1000
1500
2000
2500
3000
3500
mass of elements on filter by ICP-MS, ng


Ni
Teflon
Ur,DIR
r-RSS
r-Bias
Ur,GUM
300%
250%
200%
150%
100%
50%
0%
Relative expanded uncertainty , U_r
m_{limit}=1100 ng
$R^2 = 0.42$
100
200
300
400
500
600
mass of elements on filter by ICP-MS, ng


Cr
Teflon
Ur,DIR
r-RSS
r-Bias
Ur,GUM
R² = 0.00
100%
75%
50%
25%
0%
100
200
300
400
500
600
700
800
Relative expanded uncertainty , U_r
mass of elements on filter by ICP-MS, ng


Cu
Teflon
Ur,DIR
r-RSS
r-Bias
Ur,GUM
R² = 0.94
160%
140%
120%
100%
80%
60%
40%
20%
0%
0
1000
2000
3000
4000
5000
6000
Relative expanded uncertainty , U_r
mass of elements on filter by ICP-MS, ng


Mn
Teflon
Ur,DIR
r-RSS
r-Bias
Ur,GUM
180%
160%
140%
120%
100%
80%
60%
40%
20%
0%
Relative expanded uncertainty , Ur
R² = 0.87
0
500
1000
1500
2000
mass of elements on filter by ICP-MS, ng


Mo
Teflon
Ur,DIR
r-RSS
r-Bias
Ur,GUM
100%
75%
50%
25%
0%
Relative expanded uncertainty , Ur
R² = 0.80
0
100
200
300
400
500
600
700
mass of elements on filter by ICP-MS, ng

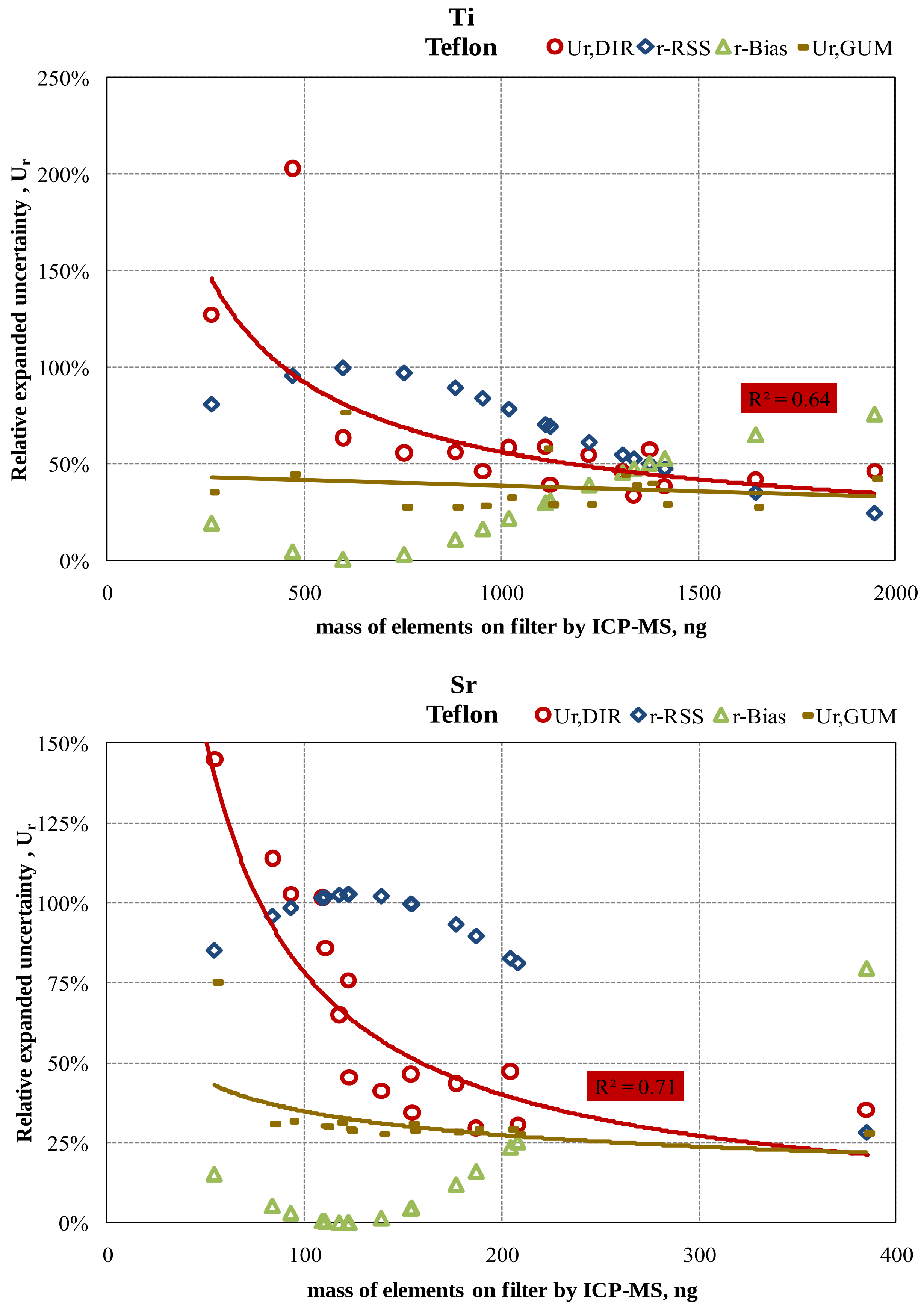


Figure 11: Comparison of $U_{r,GUM}$ and $U_{r,DIR}$ for Teflon filters. m_{lim} denotes the limit values of EU Directives and calculated by assuming 55 m^3 sampling air

4 Conclusion

1) The linear calibration of EDXRF using loaded filters were found to be site and filter independent for Pb, Mn, Fe, Cu, Ti and Zn. Ca was found to be site independent, but, filter type dependent. For QMA filters, the site effect was evidenced for K, As, Ni, Ti, and V. Teflon filters are more appropriate than QMA filters to analyze elements by EDXRF. For Teflon filters, the linear calibration gave reasonably good results if calibration filters came from a similar site. However, high deviations from certified values of the NIST 2783 appeared by linear calibration for Teflon filters, which can be attributed to different PM composition, filter material or PM cut-off. The standardless EDXRF analysis was found to be more efficient than linear calibration for the quantification of trace elements. This calibration method is filter type and sampling site independent. For Teflon filters, the standardless EDXRF analysis showed better results than linear calibration except for As, Co and V. For QMA filters, the standardless EDXRF analysis showed better results than linear calibration except for Cr and V. Cd, Sn and Sb could not be analyzed, neither by the standardless EDXRF analysis nor the linear calibration in the studied samples. The linear calibration with loaded filters can be used to analyze filters collected in the same/similar sites for Teflon filters.

2) According to the evaluated detection limits, the standardless EDXRF analysis has been found capable to determine Ni and Pb, but not Cd and As, at concentrations close to the Limit Values of EU Directives (2004, 2008). Furthermore, the Teflon filters were found to have lower detection limits than quartz ones, probably resulting from less impurities and smoother filter surface.

3) The agreement between ICP-MS and standardless EDXRF results for Teflon filters were found to be higher than for quartz ones. The differences between standardless EDXRF values and ICP-MS values are lower for Teflon filters than for quartz filters. This result supports the previous finding. Conversely to linear calibration, As, V and Co could not be analyzed by standardless EDXRF analysis.

4) The GUM measurement uncertainties of standardless EDXRF analysis were found independent of elemental mass, generally around 30%. Net intensity, I_{net}, was identified as one of the major contributors, with higher contribution at low concentrations. The background contribution to I_{net} was higher than intensity of element, I. At very low concentrations, the contribution of I_{net} increased because of worsened repeatability of I. The ratio of counts to mass of element was found to be one of the main contributors (12%). The excited area, A, deposited area, A_d, and PM mass on filter, m_{PM}, were found to be important contributors. However, these parameters also had negative contribution coming from the correlations between A and m_{PM} and between A_d and m_{PM}. The GUM uncertainties of Teflon filters were the lowest among all filters.

5) The field uncertainties of standardless EDXRF analysis decreased with elemental masses. Mass threshold for which GUM and field uncertainties were equal could be found for all elements except Cr, K, Mg for all types of filter and Ti for quartz filters. The elemental mass thresholds were lower for Teflon filters than for quartz ones. At higher elemental masses than these thresholds, the proposed model equation for estimating GUM uncertainty has demonstrated its validity and be used for whatever future filter analysis.

6) The DQO of the EU Directive for Pb was met for all types of filter even at lower concentrations (23 ng/m^3) than the Limit Value. Only for Teflon, field uncertainty for Ni is likely to comply with the DQO. However, more tests need to be performed at concentration close to the Limit Value to confirm the result of this study. For As, the best results can be achieved by analyzing Teflon filter if using with linear calibration. The resulting relative expanded uncertainty was 45 % at lower concentration (1 ng/m^3) than the Limit Value. It is likely that at the Limit Value the DQO can be met for As. Cd could not be quantified most probably due to low concentrations, and further tests at the Limit Value are required. The

EMEP DQO was met for Cu (82 ng/m^3 for Teflon) and Zn (273 ng/m^3 for quartz filter), but, not for Cr.

As the overall result of this study, EDXRF can be considered as an alternative method to ICP-MS for measurements of PM-bound elements, particularly on Teflon filters. The European legislative requirements of Pb could be met for whatever filters type. The European legislative requirements of Ni and As are likely be met, but, it is unknown for Cd. The EMEP requirements can be met for Cu and Zn, but not for Cr. EDXRF can also be used to measure elements for source apportionment purposes. Calibrating the instrument by certified matrix matched standards on filter could produce better results, particularly for As, V and Co, even at low concentrations.

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Abstract

Energy Dispersive X-ray Fluorescence (EDXRF) was compared to Inductively Coupled Plasma Mass Spectrometer (ICP-MS) for the measurements of elements in particulate matter (PM_{10}). Lead (Pb), arsenic (As), nickel (Ni) and cadmium (Cd)) and the ones included in the EMEP programme, namely copper, chromium and zinc were tested. Other elements such as magnesium, aluminium, silicon, sulphur, chloride, potassium, calcium, titanium, vanadium, iron, cobalt, manganese, bromide, strontium, molybdenum, tin and antimony, which are essential for source apportionment studies, were also tested. PM_{10} samples collected at different sites on several types of filter were analyzed using both EDXRF and ICP-MS. As the overall result of this study, EDXRF can be considered as an alternative method to ICP-MS for measurements of PM-bound elements, particularly on Teflon filters. The European legislative requirements of Pb could be met for whatever filters type. The European legislative requirements of Ni and As are likely be met, but, it is unknown for Cd. The EMEP requirements can be met for Cu and Zn, but not for Cr. EDXRF can also be used to measure elements for source apportionment purposes.

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