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Review

Roles of chemical metrology in electronics industry and associated environment in Korea: A tutorial

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ABSTRACT

Chemical metrology is gaining importance in electronics industry that manufactures semiconductors, electronic displays, and microelectronics. Extensive and growing needs from this industry have raised the significance of accurate measurements of the amount of substances and material properties. For the first time, this paper presents information on how chemical metrology is being applied to meet a variety of needs in the aspects of quality control of electronics products and environmental regulations closely associated with electronics industry. For a better understanding of the roles of the chemical metrology within electronics industry, the recent research activities and results in chemical metrology are presented using typical examples in Korea where electronic industry is leading a national economy. Particular attention is paid to the applications of chemical metrology for advancing emerging electronics technology developments. Such examples are a novel technique for the accurate quantification of gas composition at nano-liter levels within a MEMS package, the surface chemical analysis of a semiconductor device. Typical metrological tools are also presented for the development of certified reference materials for fluorinated greenhouse gases and proficiency testing schemes for heavy metals and chlorinated toxic gas in order to cope properly with environmental issues within electronics industry. In addition, a recent technique is presented for the accurate measurement of the destruction and removal efficiency of a typical greenhouse gas scrubber.

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1. Introduction

The advance of a country entails changes and advances in its industrial structure and subsequently those in the national

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measurement standards. In Korea, industrial sectors such as steel, automotive, petroleum chemistry, and construction led the national economy until the 1990s. At this period, Korea Research Institute of Standards and Science (KRISS), the national metrology institute of Korea, has met such needs by providing chemical metrological standards such as a suite of certified reference materials (CRMs) to a wide range of industrial demands and national agenda. Electronics technology has rapidly transformed and led the entire industry of Korea since 1990. In such industrial environments, KRISS are playing a pivotal role in research and development of chemical standards relevant to electronics industry of Korea. The electronics industry deals primarily with semiconductor materials, electronic displays (e.g., liquid crystal display; plasma display panel), nanomaterials, etc. Extensive roles of chemical metrology in electronics industry involve high yields and quality controls of products, environmentally friendly management, and regulatory sectors closely relating to the international trade of industrial products.

In order to pursue the demands for higher product yields and better quality control, a variety of CRMs are required, particularly for thickness determinations, surface chemical analyses, and gas analyses. A number of CRMs have also been essential to environmental metrology due to the restriction of the use of hazardous substances in electrical and electronic equipment (RoHS). Examples include CRMs for a number of gases such as NO_x, SO_2, HCl, HF, and volatile organic compounds and those for waste environmental measurement. International and domestic regulatory sectors pose strict regulations on the production of emerging greenhouse gases generated from electronics industry such as perfluorocompounds (PFCs) that include CF_4, NF_3, and SF_6. Any measurement results would be considered appropriate, only when verified procedures such as International Organization for Standardization (ISO), American Standard Testing Methods (ASTM), CRMs, and proficiency testing (PT) schemes for laboratory personnel are sufficiently met.

In the current literature, it is very difficult to find the organized information on why and how much chemical metrology is critical for sustaining and advancing electronics industry. For the first time, we present a comprehensive understanding of how chemical metrology is playing important roles in supporting electronics industry by presenting recent case studies in regard to quality controls and associated environmental issues. For a better grasp of the entire picture, typical examples are demonstrated with an emphasis on the development and dissemination of measurement standards such as certified reference materials and on the conducting proficiency testing schemes for a variety of chemical measurement activities as common practices in electronics manufacturing industry in regard to heavy metals, greenhouse gas, and toxic acid gas. Other metrological applications were also briefly discussed, such as the precise measurement of gas composition inside of the internal nano-liter cavity of a micro-electro-mechanical system (MEMS) package, the surface chemical analysis of a semiconductor material, and the accurate determination of destruction and removal efficiency of a typical greenhouse gas scrubber.

2. Chemical metrology for quality control and technology innovation

2.1. Development of measurement techniques and various certified reference materials for surface chemical analysis

Surface composition and its in-depth distribution of constituent materials are important issues in the advanced industries. Recent international technology roadmap for semiconductor showed that the reliable depth profiling analysis of doping elements in the shallow junction region and the thickness measurement of ultra-thin gate oxides are required for the next generation of semiconductor devices. X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) are the main techniques for surface chemical analysis. SIMS is useful for the quantification and depth profiling analysis of minor impurities in the fields of semiconductor and new materials because of its high sensitivity and detection capability of all elements including hydrogen. XPS and AES are mainly used for the quantification and depth analysis of major components. In addition, diverse focused ion beam (FIB) based techniques such as FIB microscope and dual platform of FIB with sequential or simultaneous scanning electron microscope (SEM) imaging has been widely used, most significantly in the field of inspection of integrated circuits and electronic devices manufactured by the semiconductor industry in order to derive in depth information [1–3].

International Organization for Standards (ISO) and Versailles Project on Advanced Materials and Standards–Surface Chemical Analysis (VAMAS–SCA) have started to systematically research on international standardization of surface chemical analysis [4]. In addition, international comparisons of surface analysis by National Metrology Institutes (NMIs) have been launched by the Surface Analysis Working Group (SAWG) of the Consultative Committee for Amount of Substance (CCQM) since 2004. The thickness determination of ultra-thin SiO_2 thin films on Si (100) and Si (111) substrates was the first key comparison (KC) through CCQM-K32 by SAWG [5,6]. XPS was found to be the most powerful technique for the determination of the thickness of a gate oxide in the thickness range of nanometer and sub-nanometer [7–9]. An international key comparison on measurement of composition of a thin Fe–Ni alloy film (CCQM-K67) was proposed and recently completed by KRISS, the coordinating laboratory [10–12].

KRISS developed an ion beam sputter deposition system to grow various thin film CRMs [13]. The target materials are sputtered by Ar ions and deposited on Si wafers using a rotating substrate holder. Many kinds of binary alloy films and multilayer films can be grown by this system. The surface composition and chemical state of the films grown in the deposition system can be analyzed by in-situ XPS analysis. Three kinds of thin film CRMs have been developed by KRISS for the standardization of surface chemical analysis as shown in Table 1.

The multilayer CRMs are usually used to optimize the analysis conditions and to evaluate the depth resolution. ISO 14606 descri-

Table 1
The KRISS reference materials of thin film for surface chemical analysis.

Use	KRISS CRM identifier [44]	Surface structure
Multilayer thin films for depth profiling	103-04-001	Ta_2O_5/SiO_2 multilayer thin film
	103-04-002	Ta_2O_5/Ta multilayer thin film
	103-04-003	Si/GaAs doped Si multiple delta-layer
	103-04-004	Si/B-doped Si multiple delta-layer
	103-04-007	Si/Ge multiple delta-layer
Quantitative analysis by XPS and AES	103-04-011	Pt–Co alloy thin film
	103-04-012	Fe–Ni alloy thin film
	103-04-013	W–Si alloy thin film
Quantitative analysis of B in Si by SIMS	103-04-031	B doped Si thin film

Notes: XPS = X-ray photoelectron spectroscopy; AES = Auger electron spectroscopy; SIMS = secondary ion mass spectrometry.

bes the guidelines for the optimization of sputter depth profiling parameters using super-lattices and other multilayered systems in order to achieve optimum depth resolution in XPS, AES and SIMS depth profiling [14]. ISO 20341 specifies a method for estimating depth resolution parameters which are the leading edge decay length, the trailing edge decay length and the Gaussian broadening in SIMS depth profiling [15]. Recently, a new method to calibrate SIMS depth scale using a multiple delta-layer CRM was established by cooperation between KRISS and NIST [16]. A SIMS depth profile of the Si/Ge multiple delta-layer CRM (KRISS CRM 103-04-007) is presented in Fig. 1. The SIMS depth scale can be traceable to the length unit from the certified thickness [17]. The certified value of the Si/Ge multiple delta-layer with a size of 10 mm × 10 mm (KRISS CRM 103-04-007) was 234.1 nm with an expanded uncertainty of 0.3 nm at $k=1.96$. The main uncertainty sources were associated with the thickness measurements of the test sample with the minor contributions of the certified thickness values of the reference specimens.

XPS and AES are, after careful calibration, useful methods for quantitative surface compositional analysis of multi-component systems. Although, the relative sensitivity factors (RSFs) determined from pure metals are typically useful for the quantification of alloy materials, the matrix effects due to the atomic density, the attenuation lengths of electrons, electron scattering correction factor and the electron backscattering factor (particularly for AES) in the matrix materials must be taken into account [18,19]. Alloy thin film CRMs can be used to obtain a calibration line for the quantitative analysis of binary alloys that can minimize the matrix effects using pure element reference materials. Fe–Ni alloy films (KRISS CRM 103-04-012) has been recently studied.

The quantity and in-depth distribution of doping elements are important factors to determine the electrical property of semiconductor devices. Although SIMS is one of the most powerful techniques for the in-depth analysis of doping elements, quantitative SIMS analysis of minor impurities is restricted by the difference in ionization probability due to matrix effects. SIMS quantification process is therefore performed with a standard reference material of which matrix is identical to the analytes [20,21]. ISO 14237 describes a method for the quantification of B in Si using a secondary reference material in daily analyses [22]. In this standard, NIST SRM-2137 is recommended as the only CRM for the quantification of B in Si [23]. As shown in Fig. 2, B-doped Si thin film (KRISS CRM 103-04-004) certified by inductively coupled plasma mass spectrometry with an isotope dilution method shows a uniform in-depth distribution of B concentration [24].

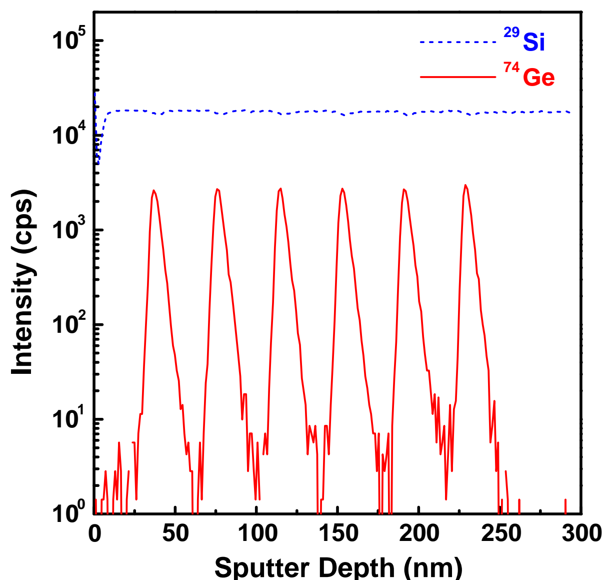

Fig. 1. A SIMS depth profile of Si/Ge multiple delta-layer. The unit of intensity is counts per second (cps) [17].

2.2. Development of a measurement technique for gas composition in the nano-liter cavity of a MEMS package

The importance of chemical metrology is being recognized even to the emerging nanotechnology in electronics industry. As the dimensions of electronic devices such as semiconductor chips become more and more minimized, a micro-electro-mechanical system (MEMS), an innovative technology, has received strong attention. The MEMS is defined as a device that consists of integrated mechanical constituents on the nano-scale. KRISS in cooperation with Samsung Electronics Corporation Ltd. developed a novel gas analysis system to be capable of identifying the accurate internal capacity of a MEMS package as well as of estimating the absolute amount of substance [25]. For this application, the associated uncertainties of each component were also evaluated in the trapped atmosphere and the sampling limit of the system. A test specimen of the MEMS package is illustrated in Fig. 3. The

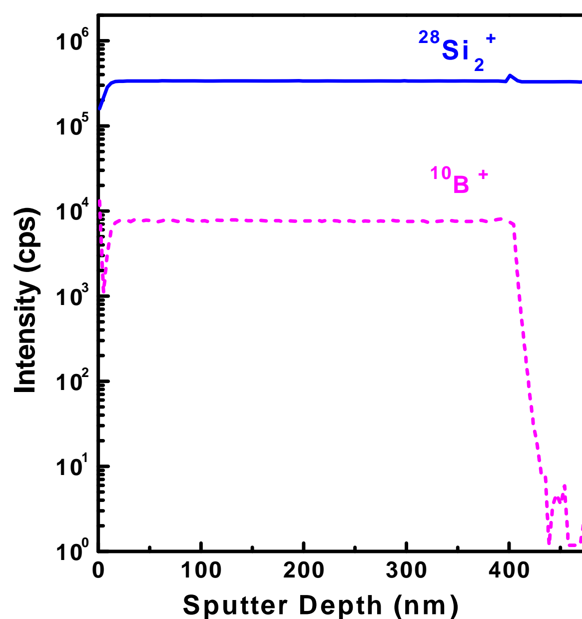

Fig. 2. SIMS depth profile of B-doped Si thin film CRM.

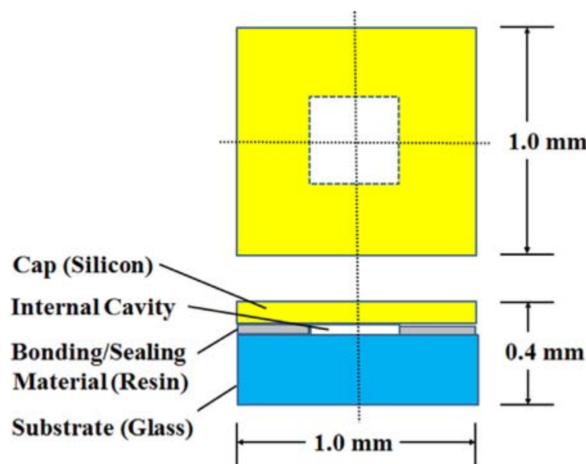

Fig. 3. Schematic illustration of a test specimen of the MEMS packaging.

external dimension of the MEMS package was approximately 1.0 mm × 1.0 mm × 0.4 mm. Its internal cavity was 6 nL with detection limit of 1.1 nL under the internal cavity pressure of 0.96 atm, slightly lower than the ambient pressure (1.0 atm). With regard to uncertainty, test results from a single test using the 5 virtually identical specimens indicated that the gas composition in the internal nano-liter cavity of the MEMS package was comprised of 94.63 cmol mol^{-1}, 3.33 cmol mol^{-1}, 2.04 cmol mol^{-1} for N_2, Ar, and H_2, respectively. The relative expanded uncertainties (k=1) for N_2, Ar, and H_2 were 4.3%, 8.6%, 3.6%, respectively. The main uncertainty sources were the variability in virtually identical samples simultaneously used for a single test and the variability of response signal (current) for each gas component (approximately 2% at a coverage factor of 1). This shows the potential applicability as a sealing evaluation tool. Innovations of MEMS are expected to have significant impacts on minimizing size, reducing cost and improving the performance of various materials in electronics industry.

3. Chemical metrology for solutions to environmental regulations associated with electronics industry

Since a number of environmental contaminants discharged from electronics industry directly affect the survival of humans and biota, many central and local governments dealing with environmental affairs across the world have placed the permissible concentration limits for a number of pollutants under associated regulations. Once the level of a contaminant exceeds its allowable concentration range, legal restrictions in various forms such as fines or reduction of working days can be imposed on the party in charge. Accordingly, companies responsible for the release of contaminants need to install and operate emission reduction facilities based upon such regulations and to subsequently monitor changes to contaminant concentrations. To ensure the reliability of measurement results, a systematic procedure would be necessary for each analytical measurement system that involves calibration, checking, and management.

3.1. Development of certified reference materials for environmental regulations against hazardous metals

Environmental regulations have posed technical barriers on the international trade of electric and electronic products and automotive. Such examples include RoHS and the proposal for a directive on waste from Electric and Electronic Equipment (WEEE) established by European Commission (EC) [26,27]. Levels of hazardous metals regulated by RoHS are 100 mg kg^{-1} for Cd and 1000 mg kg^{1} for Cr^{6+}, Hg, and Pb. Main constituents of electric and electronic products are metals and polymer resins. Elemental analyses of the polymer resins are being conducted extensively by polymer production companies, testing laboratories, and regulation sectors. Although there are no approved analytical methods by ISO, United States Environmental Protection Agency (US-EPA) has proposed relevant methods [28,29]. Such circumstances have caused technical problems in evaluations of analytical results between interested parties.

Ideal tools for enhancing the mutual reliability of measurement results are CRMs. Availability of the CRMs for metal analysis in polymer resins was limited to date. A certified mixture of As, Cr, Cd, Cl, Cr, Hg, Pb, S, Sb at low and high mass fractions in two polyethylene (PE) CRMs of pellet type (ERM®-EC680k and ERM®-EC681k) are being provided by Institute for Reference Materials and Measurements (IRMM) [30]. Now available are mixtures of Cd, Cr, and Pb or Cd, Cr, Hg, and Pb at low and high mass fractions in acrylonitrile–butadiene–styrene-copolymerisate (ABS) or polyvinyl chloride (PVC) or polypropylene (PP) in pellet or disc types (NMIJ CRM 81XX-a) certified by National Metrology Institute of

Table 2
Results of mass fractions of metals contained in the KRISS reference materials of polypropylene.

KRISS CRM identifier [44] analyte	Mass fraction of analyte [mg kg^{-1}]				
	113-01-001	113-01-002	113-01-003	113-01-004	113-01-005
As	≤ 1.0	16.9 ± 2.8	123 ± 3.6	397 ± 12	773 ± 28
Cr	≤ 0.5	16.7 ± 0.5	146 ± 2	482 ± 10	976 ± 33
Hg	≤ 1.5	16.5 ± 2.0	140 ± 8	483 ± 29	944 ± 31
Pb	≤ 0.1	16.9 ± 0.8	145 ± 4	476 ± 7	948 ± 43
Zn	≤ 1.0	16.6 ± 1.1	149 ± 8	482 ± 22	994 ± 39
Cd	≤ 1.0	1.71 ± 0.09	14.5 ± 0.3	49.6 ± 1.4	96.5 ± 3.0
Ba	ND	39.4 ± 1.2	348 ± 5.5	1150 ± 11	2290 ± 76

Note: X and U denote a value and its expanded uncertainty at a confidence level of 95%.

Table 3
Homogeneity test results of the KRISS certified reference materials of Cd and Pb in polypropylene resins.

KRISS CRM identifier [44]	Analyte	Mass fraction			RSD [%]
		Value [mg kg^{-1}]	k	U [mg kg^{-1}]	
PPL (113-01-003)	Cd	14.9	2.2	0.2	0.68
	Pb	144.3	2.2	2.7	0.76
PPH (113-01-005)	Cd	98.2	2.3	4.04	1.79
	Pb	959	2.3	41	1.90

Notes: k is coverage factor; U is expanded uncertainty; RSD (%) is relative standard deviation; PPL and PPH are low and high mass fractions of Cd and Pb in polypropylene resins, respectively.

Japan (NMIJ) [31]. In addition, a mixture of Pb, Br, Cd, and Cr in ABS (BAM-H010) is also available [32].

KRISS developed PP CRMs of pellet and disc types by requests of industry. Presently, five levels of mass fractions of metals in PP were prepared as shown in Table 2. In order to certify PP CRM-candidates, these candidates were pretreated using a microwave-assisted acid digestion method and are being analyzed by isotope dilution mass spectrometry (IDMS) and inductively coupled plasma/optical emission spectrometry (ICP/OES). Measurement uncertainties about the mass fractions of each element in PP were evaluated as shown in Table 2. For instance, expanded uncertainties for each element contained in KRISS CRM 113-01-002 were 16.9 ± 2.8 mg kg^{-1} for As, 16.7 ± 0.5 mg kg^{-1} for Cr, 16.5 ± 2.0 mg kg^{-1} for Hg, 16.9 ± 0.8 mg kg^{-1} for Pb, 16.6 ± 1.1 mg kg^{-1} for Zn, 1.71 ± 0.09 mg kg^{-1} for Cd, and 39.4 ± 1.2 mg kg^{-1} for Ba. Of the 4 different levels (KRISS CRM 113-01-002, 113-01-003, 113-01-004, and 113-01-005), CRM 113-01-002 contain the lowest mass fractions of the elements except the blank (KRISS CRM 113-01-001). Main sources of uncertainties were associated directly with reproducibility of sample preparation, pretreatment and recovery, and with element concentrations in working standard solutions.

Besides, KRISS also established some CRMs for toxic metals such as Cd and Cr in polypropylene for seven samples at two different mass fraction levels using the instrumental neutron activation analysis [33].

In 2006, KRISS conducted two proficiency testing (PT) schemes for the measurements of Cd and Pb contained in polymer resins for the laboratories of electric, electronic and automotive industries, which were accredited by Korea Laboratory Accreditation Scheme (KOLAS). A total of 31 testing laboratories participated in this PT. Proficiency testing materials were 2 PP CRM-candidates as represented by PPL and PPH which denote low and high concentrations of Cd and Pb in polypropylene, respectively, as shown in Table 3. To determine the

reference values, procedures were adopted which consist of the random selection of 10 sample bottles from a total of 300 and 450 sample bottles for the low and high levels of metals in polypropylene samples denoted as PPL and PPH, respectively, followed by chemical analyses based on isotope dilution mass spectrometry (IDMS) and inductively coupled plasma/optical emission spectrometry (ICP/OES), and subsequently by the evaluation of homogeneity between the testing samples (Fig. 4). The results from the PT of Cd and Pb in the PP samples showed that the mean values of results from each participant were in good agreement with the reference values of KRISS within 2% and 1.5% for Cd and Pb, respectively. However, in case of Cd, 14 laboratories for PPL samples and 10 laboratories for PPH samples deviated greater than 10% from the reference values. In case of Pb, 8 laboratories indicated more than 10% of errors for both PPL and PPH samples. A variety of determination methods were employed by each laboratory, including EPA 3051, 3052(B), 6010B, EN 1122, ISO 6101-2, IEC 62321, and ASTM D 4004. While 18 laboratories adopted microwave assisted acid digestion methods, others employed dry ash or open methods. In short, widely varying methods are utilized by different laboratories for the PT samples and the target elements. Such circumstances strongly suggest the needs for the standardization of decomposition methods and measurement analyses.

3.2. Development of certified reference materials for environmental regulations against atmospheric emissions of perfluorocompounds

The Kyoto Protocol was ratified on the mitigation of greenhouse gas emissions in 1997 and has come into effect on 2005. Typical perfluorocompounds (PFCs) such as CF_4, including SF_6 and NF_3 used in the electronics industry are fairly stable and do not occur naturally but are released primarily from semiconductor and aluminum manufacturing industry. Semiconductor processing typically involves with PFC gases for wafer etching and chamber cleaning processes for chemical vapor deposition (CVD) [34–37]. Since these gases are emitted to ambient air, potentially leading to the long-term greenhouse effect, voluntary base regulations are being imposed on these gases by electronics companies in Korea.

Electronics industry has been well developed across Northeast Asia that includes Korea, Taiwan, Japan and China. Effective reductions of PFCs from emission sources depend heavily upon the evaluations of associated manufacturing processes and reduction technologies. To meet such needs, KRISS developed CRMs for the analysis of NF_3, SF_6 and CF_4 at the nominal mole fractions of 100 μmol mol^{-1} that represent emission sources of those PFCs and performed a key comparison through CCQM-K15 in 2003 [38].

In 2005 and 2006, KRISS have developed CRMs and analytical methods for ambient air, by establishing accurate evaluation methods readily applicable to field situations. As a result, KRISS is capable of determining SF_6 and CF_4 at the levels of 5 pmol mol^{-1} and 80 pmol mol^{-1}, respectively. The CRMs developed for the two gases were prepared at trace levels using a gravimetric method to be capable of maintaining international traceability. Consequently, KRISS has disseminated the CRMs for PFCs to the Korea Meteorological Administration (KMA) and electronics companies for the reliable measurements of these gases in the ambient air and facility environments, respectively.

In general, in-house reference gas mixtures at trace concentrations were manufactured through several dilution processes after purity analyses of source and matrix gases. The reference gases at each dilution step were analyzed using gas chromatographic techniques (GC) with various detectors such as thermal conductivity detector (TCD), atomic emission detector (AED), mass spectrometer detector (MSD), and electron capture detector (ECD). Subsequently, the reference gas mixtures were verified by confirming internal consistency in the concentrations of a target compound between the prepared cylinders for com-

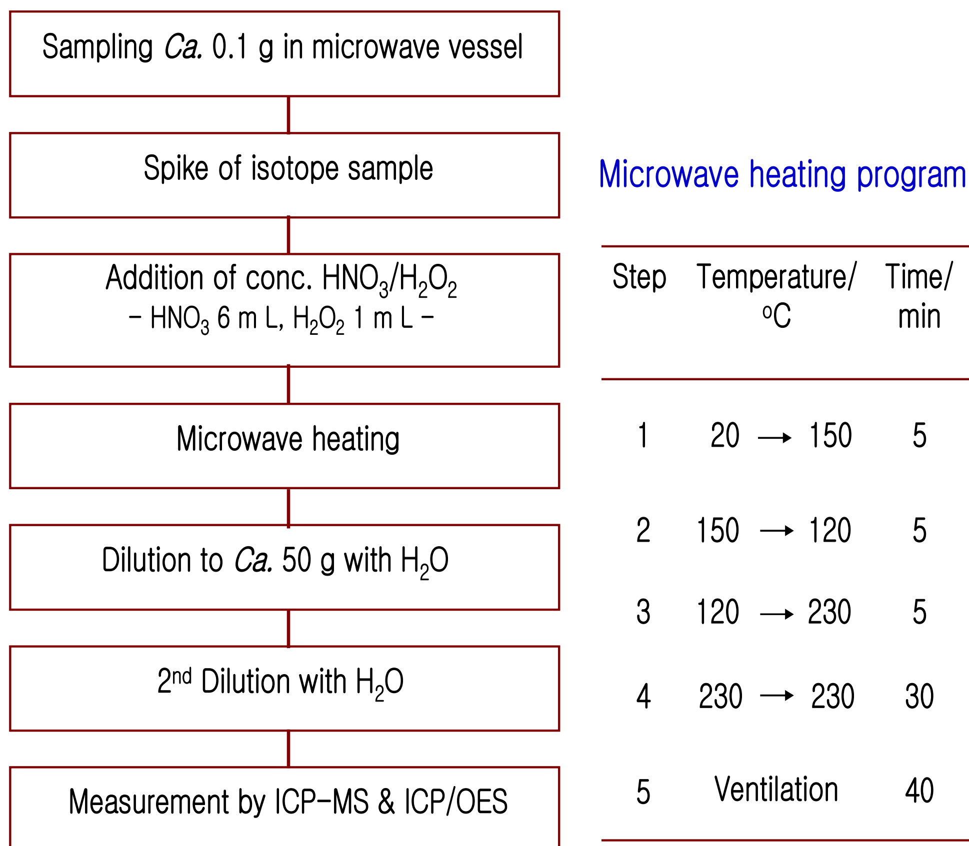

Fig. 4. Sample pretreatment procedure of PP resins for ID-ICPMS and ICP/OES.

parison. The internal consistency testing for the concentrations of SF_6 in the finally diluted cylinders were conducted with a temperature-programmed, pre-concentration and elution device in line with GC–ECD.

In addition, Table 4 demonstrates the measured values of mole fraction of SF_6 with combined uncertainties expressed in expanded uncertainties. The main sources of uncertainty originated from the reproducibility in multiple dilution steps from high purity SF_6 to the target concentrations using gravimetric preparation and the reproducibility of the peak areas for SF_6 from pre-concentration at low temperatures and subsequent analysis using GC–ECD.

Besides, KRISS reported that variation of argon (Ar) content in CRMs for synthetic air mixtures could undermine accuracy for precise and accurate the determination of CO_2 in ambient air from the research attempts to resolve some metrological issues of carbon dioxide (CO_2) in ambient air nationally monitored by KMA [39].

3.3. Development of a measurement technique for the accurate evaluation of gas scrubber's performance to prevent greenhouse gas emissions

In order to reduce the emissions of perfluorocompounds (PFCs), electronics companies in Korea have been installing greenhouse gas scrubbers in manufacturing facilities. The proper management of PFC emissions from the sources requires accurate evaluations on the performance of the gas scrubbers. According to the guideline presented by the International Panel on Climate Change (IPCC), the extent of emission reduction of PFCs can be evaluated by testing the performance of a greenhouse gas scrubber as an emission control technology [40].

Motivated by the request of a liquid crystal display (LCD) manufacturing company, KRISS recently developed and proposed a method to evaluate the performance of a gas scrubber in terms of destruction and removal efficiency (DRE) especially for fluorinated greenhouse gases such as PFCs [41]. The measurements of the flow rates of target samples were made using the injection of a KRISS primary standard reference gas of high-purity helium (KRISS CRM 112-06-004). The accurate partial pressure analysis was conducted using a precision gas mass spectrometer (gas-MS) (Finnigan MAT 271). The sampling system of the process gases including SF_6 or NF_3 are illustrated in Fig. 5. KRISS collected and analyzed gas samples at the inlet and outlet of the scrubber connected to the chemical vapor deposition (CVD) chamber cleaning chamber. As shown in Table 5, the analytical results were computed based on a mole fraction. The increases in the concentrations of N_2, O_2 and Ar were due to the intake of ambient air used for combustion of fuel (e.g., natural gas) usually used in burner-type scrubbers. The flow rates were measured indirectly from the difference in the concentrations in helium at the inlet and outlet because an increase in the quantity of the air would cause a decrease in the He concentrations. The relative expanded uncertainty ($k=2$) for the mole fraction of each species are given in Table 5. The uncertainty estimates were 5% for H_2 and CO_2, 1.0% for He and Ar, 0.3% for N_2 and O_2, 2% for NF_3 at the inlet and 5% for NF_3 at the outlet. The DRE measured for this example was 95.6%. The relative expanded uncertainty about the DRE at a coverage factor of 2 was estimated 2%. When it is assumed that there is no error in representative gas sampling and transport using a highly pressurized inert gas cylinder from the test field to the KRISS laboratory, the main source of uncertainty about the DRE was the

Table 4
Results of certified values and associated expanded uncertainties of SF_6 mole fractions in the KRISS gas cylinders.

Cylinder identifier of KRISS primary standard gas mixtures	SF_6 in air [pmol mol^{-1}]	U ($k=2$) [pmol mol^{-1}]
YA001797	2.007	8.5×10^{-3}
YA001802	4.012	8.9×10^{-3}
YA001805	7.053a	9.7×10^{-3}
YA001827	9.216	10.0×10^{-3}

Notes: U is expanded uncertainty at a coverage factor (k) of 2; A recent KRISS CRM catalog indicates that CRM 12-01-026 is available for SF_6 in air at 50 nmol mol^{-1} with relative expanded uncertainty of 1% at a coverage factor of 2 [44].

Table 5
Results of mole fraction composition in the sample gases at the inlet and outlet of the scrubber tested (adapted from [32]).

Analyte	Inlet		Outlet	
	Mole fraction [cmol mol^{-1}]	U_{rel} [%] ($k=2$)	Mole fraction [cmol mol^{-1}]	U_{rel} [%] ($k=2$)
H_2	0.0041	5	0.0328	5
N_2	98.40	0.3	82.33	0.3
O_2	0.0318	0.3	16.62	0.3
Ar	0.0036	1.0	0.686	1
CO_2	0.551	5	0.0761	5
He	0.952	1	0.250	1
NF_3	0.0583	2	0.00067	5
Total	100.00		100.00	

Note: U_{rel} is relative expanded uncertainty in percentage about measured mole fraction at a coverage factor (k) of 2.

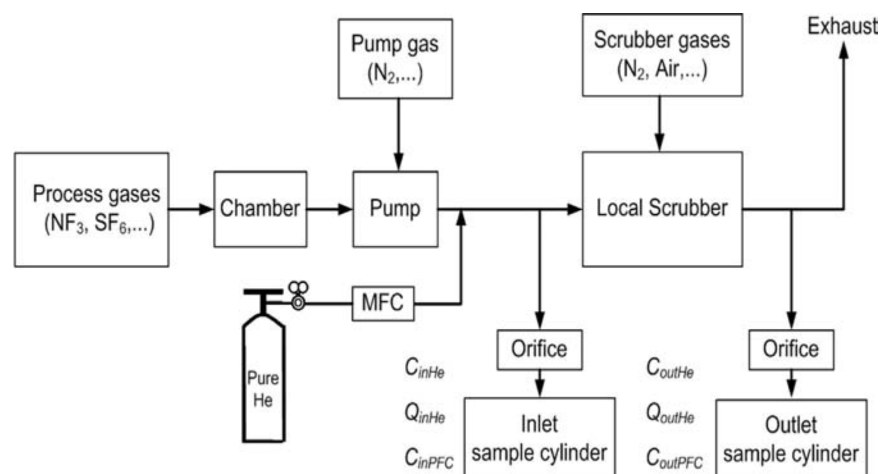

Fig. 5. Schematic diagram of the gas sampling system from a scrubber [41].

variation in response signal (current) for each gas component when using the precision gas-MS operated at the KRISS laboratory. However, not just uncertainties associated with measurement of mole fractions of gas components but also uncertainties about temperature and pressure measured would be main sources of the uncertainty of DRE at a field test environment frequently using Fourier transform infrared spectrometers (FTIR) or quadruple mass spectrometers (QMS). Further research is continued for developing appropriate methods for the determination of DREs for PFCs under various conditions.

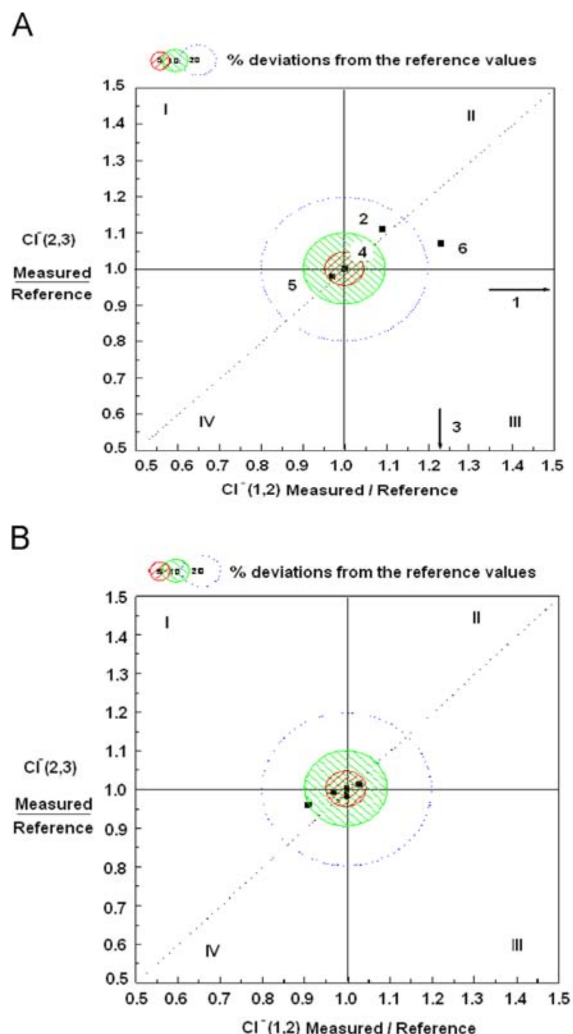

Fig. 6. Youden plot for the measurement results for Cl^- from the first (A) and the second proficiency testing schemes (B).

3.4. Development of proficiency testing schemes for improving practical capability to measure a toxic gas in manufacturing environments

KRISS organized and conducted proficiency testing (PT) schemes on HCl, a potential atmospheric pollutant released from electronics industry, in coordination with atmosphere-associated laboratories in Korea. The measurement methodology used by the participants of this PT was based on the procedures that consist of quantitative conversion of HCl in the gas phase into Cl^- in the absorbing solution, followed by analysis of Cl^- concentrations using ion chromatography (IC) [42].

To evaluate the reliability of the measurement results, PTs were carried out in the two stages. KRISS prepared 3 types of samples, distributed duplicate samples for each type to each participating laboratory. Reference solutions were utilized for the PTs on the determination of Cl^- concentrations. KRISS checked the stability of samples under the PTs within the uncertainties of the reference concentrations within a predetermined measurement period. The reference concentrations used for the PTs were 0.35 L^{-1}, 0.80 L^{-1}, and 1.20 mg L^{-1}. A total of 6 laboratories participated in the PTs. From the first PT results, the potential reasons for the differences in the reported values were identified. Appropriate instructions were provided to each participating laboratory in order to minimize potential differences. Subsequently, the second PT was conducted.

Fig. 6A shows the Youden plot for the results from the first PT in order to statistically evaluate the potential reasons that cause apparent deviations. The comparison results of Laboratory ID. 4 were located in the center while those of Laboratories ID's 5, 2, 6 were placed within 5%, within 20%, and out of 20% deviations from the center, respectively, suggesting the potential presence of a systematic reason. It was confirmed that the differences in the reported concentrations between the laboratories were due to errors in the steps of collecting aliquots from the reference solutions and/or dilution of the aliquots. The results of Laboratories. 1 and 3 were located in the right-hand side and lower region (III) far from the center, indicating significant

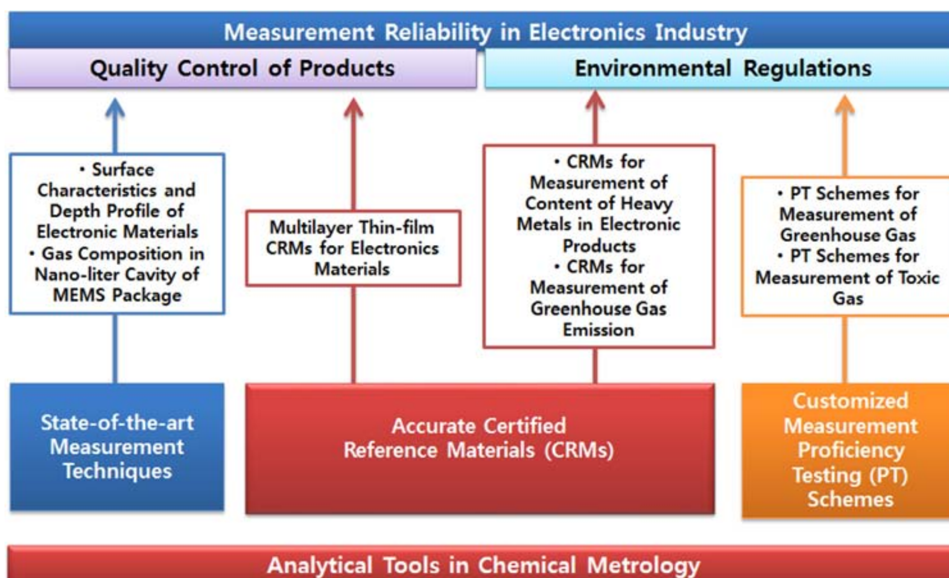

Fig. 7. Typical pathways that demonstrate practical contributions of chemical measurement tools to the demands for better measurement reliability in electronics industry.

deficiency in the measurement proficiency of the participating personnel. As presented in Fig. 6B, the results from the second PT showed noticeable improvement when compared with those from the first PT. The results from a single laboratory showed 10% deviation from the center. Overall results from the two subsequent PTs provide the following lessons. Basically, it would be nearly impossible for all participating laboratories to achieve satisfactory results through PTs. More importantly, the reliability of measured values could be improved after investigating the sources of errors or uncertainty factors systematically and providing proper instructions to solve the potential problems discovered.

KRISS also is developing analytical methods for environmental safety in workplaces within manufacturing facilities of electronics industry. KRISS recently developed a direct analytical method of arsine (AsH_3) being frequently used as a dopant as in the processing of semiconductors. This method is characterized by introduction of gas samples containing arsine into stable plasma stream, followed by gas phase oxidation of arsine with molecular oxygen in a dynamic reaction cell (DRC) equipped with an inductively coupled plasma and mass spectrometer (ICP–MS) system, followed by subsequent detection of AsO^+ ion [43]. This method demonstrated low relative expanded measurement uncertainty (0.66%) for the measurement results of traceable arsine mole fractions ($<700\ \mu g\ m^{-3}$). The main source of the uncertainty was the reproducibility in signal intensity of working standard arsine gas samples in the ICP–DRC–MS system.

4. Conclusions

The needs of quality products and increasingly stringent environmental regulations have raised the significance of measurements of chemical species that are being utilized and released from electronics manufacturing processes. This paper explored a comprehensive understanding of how chemical metrology for electronics industry can be conducive to supporting electronics industry. Typical metrological tools include the development and dissemination of certified reference materials, applications of associated measurement techniques, and comparison of measurement proficiency. With these tools, the paper demonstrated that chemical metrology can meet needs of electronic industry in order to improve quality products from electronics industry and to provide practical solutions to relevant environmental regulations (Fig. 7). Although particular needs from electronic industry and associated metrological support were demonstrated using the cases of Korea, general implications are applicable to countries where metrological or environmental research and development associated with electronics industry are active in other countries such as the United States, France, Italy, Japan, and Taipei China.

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