

High-Throughput Semiquantitative Screening of Ambient Air Samples by ORS-ICP-MS and Integrated Sample Introduction System (ISIS)

Application

Environmental

Author

Neal Julien
Midwest Research Institute (MRI)
Florida Division
Palm Bay, FL
USA

Abstract

A new method has been developed to analyze large numbers of air samples for trace metal content. To aid sample throughput, an Agilent Integrated Sample Introduction System (ISIS) was used with an Agilent 7500c Octopole Reaction System-ICP-MS operating in semiquantitative analysis mode. Using this methodology, 2,500 samples were analyzed for dissolved and extractable elemental composition in approximately 2 weeks. Instrument stability and reliability was demonstrated by good recoveries for the NIST 1643e water CRM. Data handling made use of macros to download and export sample results in a format easily imported by statistical analysis software.

Introduction

ICP-MS is unique in its ability to rapidly determine the approximate elemental composition of unknown samples using a process called “semiquantitative analysis” or “semiquant.” In semiquant, the mass spectrometer is rapidly scanned over the entire mass range, thereby detecting the response for every possible element or isotope. From these responses, semiquant can estimate the relative concentration of each element based on a table of known relative responses for all isotopes. If the concentration of a single or a few components is known, for example, an added internal standard(s), then the concentrations of the remaining

elements can be determined.

Traditionally, a limitation of semiquant has been the possibility of uncorrected polyatomic interferences leading to false positive results. While the advent of collision reaction cell (CRC) technology has significantly reduced this problem in quantitative ICP-MS, in most cases, it has not benefited semiquant in the same way. This is because semiquant must be performed with all elements acquired under identical conditions so that response factors can be interpolated across the mass range. Reactive CRC processes create new interferences and therefore cannot be used for all elements simultaneously. However, helium (He) collision mode does not create any new interferences and can be used to reduce virtually all polyatomic interferences using a process called kinetic energy discrimination. Semiquant analysis using He mode only is much less prone to interferences than traditional semiquant and can be used even in complex, unknown matrices. For these reasons, it is particularly useful in surveys where nothing is known about the possible composition of the samples, and therefore calibration for every possible element would be expensive and time consuming.

Since absolute quantitative accuracy and precision are not expected, semiquant can rely on fewer replicates and shorter integration times than quantitative analysis. In this work, the entire mass range is scanned in about 40 seconds. However, in order to take full advantage of the rapid acquisition, equally rapid sample handling is required. By using the Agilent Integrated Sample Introduction System (ISIS) in a segmented flow configuration, sample uptake and rinseout were reduced to about 20 seconds each. The result was a complete, fully automated semiquant survey of unknown samples



Agilent Technologies

in 1 minute per sample.

Midwest Research Institute (MRI)

MRI is an independent, not-for-profit research organization headquartered in Kansas City, Missouri, with laboratory facilities in Palm Bay, Florida, and Rockville, Maryland. MRI also manages the National Renewable Energy Laboratory in Golden, Colorado. The Institute performs research in energy, engineering, life sciences, national security, and defense.

Brevard Teaching and Research Laboratory (BTRL) was one of the earliest laboratories in Florida to acquire ICP-MS and has been using the technique for trace element analysis since 1991. The company was purchased by MRI in 1996 and recently acquired an Agilent 7500c to support research in bioanalytical and forensic applications.

Project Description

MRI was recently contracted to analyze 2,500 air samples collected using a SpinCon Advanced Air Sampler (Sceptor Industries, Kansas City, MO) for elemental composition. The SpinCon is a wet-concentrator air sampler designed to collect particulate matter and other airborne molecular material directly into a collection solution. The composition of the solution can be optimized to maximize recovery of specific analytes. The volume available for elemental analysis was approximately 5 mL; no information about sample composition was provided. After preliminary discussions with the client, it was determined that semiquantitative analysis would be sufficient, provided a measure of data quality could be defined and sample turnaround requirements could be satisfied. Finally, a turnaround time of 1 month was required to meet project scheduling demands.

Experimental

Materials and Methods

An Agilent 7500c ICP-MS with Octopole Reaction System (ORS) and ISIS was configured with an in-house design for rapid sample throughput (see Table 1 for operating parameters). A customized ISIS program was developed using Agilent's multi-pump module (MPM) builder software¹ to control

the ISIS valve and pumps for this application. The system was operated in a so-called "stream selection" mode to maximize sample throughput.

Calibration and check solutions were prepared from National Institute of Standards and Technology (NIST) traceable material. The instrument was calibrated before each use with a 29-component multi-element standard prepared from stock solutions obtained from SPEX Certiprep, Inc. (Metuchen, NJ).

NIST standard reference material 1643e, Trace Elements in Water, was diluted 10-fold with 1% nitric

Table 1. Instrumental Parameters for Agilent 7500c ORS ICP-MS

Parameter	Value
RF power	1500 W
Plasma gas flow	15.0 L/min
Auxiliary gas flow	1.0 L/min
Makeup gas flow	0.30 L/min
Helium (ORS) gas flow	2.0 mL/min
Sampling depth	6.0 mm
Spray chamber temperature	7 °C
Number of isotopes acquired	196
Integration time per isotope	100 ms

Sample Preparation

Air samples were collected using the SpinCon air sampler at a rate of 450 L/min directly into a 10-mL volume of a proprietary collection solution. A 5-mL aliquot was shipped to MRI (FL) and stored at 4 °C until processed.

Samples were prepared for dissolved and extractable element analysis in a final matrix of 1% nitric acid by volume. For dissolved element analyses, the sample was mixed thoroughly and a 200- μ L aliquot removed then centrifuged at 1,000 rpm for 10 minutes. A 100- μ L aliquot of the supernatant was removed and diluted to 1,000 μ L with 1% nitric acid directly into an autosampler tube. For extractable element analysis, a 200- μ L aliquot of sample was mixed with the processing reagents and shaken at room temperature for 10 minutes to simulate field processing. The sample was then diluted to a final volume of 2,000 μ L with 1% nitric acid, centrifuged at 1,000 rpm for 10 minutes, and a 1,000- μ L aliquot transferred to an autosampler tube. With this procedure, each sample produced two fractions for analysis, resulting in a total of 5,000 individual analyses.

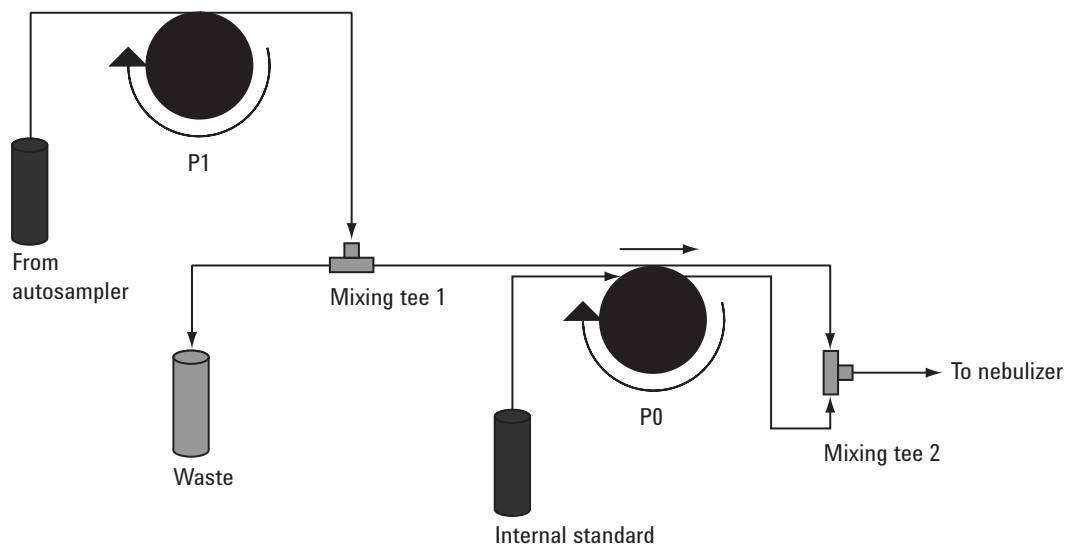
¹ Available from Agilent by special request. The MPM builder allows the user to develop sophisticated, custom ISIS applications and integrate them into routine, automated ICP-MS analysis.

ISIS Programming

In the standard high-throughput ISIS application (Figure 1), the ISIS peristaltic pump (P1) is used to rapidly deliver the sample or rinse solution to the nebulizer peristaltic pump (P0), which operates at a fixed speed. The advantages of this constant flow approach are that the plasma is never disturbed by changes in the sample loading rate and stabilization delays are minimized, since less time is wasted waiting for the pump tubing to stretch and relax, as occurs when the pump speed is changed. A drawback is that at constant flow, approximately 35 seconds are required to move the sample from mixing tee 1 to the nebulizer and allow for signal stabilization. An additional 10 seconds are required to transfer the sample from the autosampler tube to mixing tee 1. With this configuration a stable signal profile is obtained approximately 45 seconds after the autosampler probe enters a sample.

Another consideration when using the standard ISIS configuration is the time penalty incurred to flush the sample still in the pump tubing when the analysis is complete, which is in addition to the normal rinse period. The rinse time required for this application was evaluated with a 1,000- $\mu\text{g/L}$ cobalt standard. Using a cyclonic spray chamber with an internal volume of 50 mL, the rinse time to reduce the signal by three orders of magnitude ($< 1 \mu\text{g/L}$) was approximately 40 seconds.

Given the constraints of the project, higher throughput was needed. Using standard high-throughput conditions with 40-second read time, the total time required for a single sample is approximately 120 seconds (rinse in/stabilize, 40 seconds; data acquisition, 40 seconds; and rinse out, 40 seconds). Using the CETAC ASX-510 autosampler, a fully loaded tray of 270 samples (three racks with 90 samples each) with calibration and QC checks every 20 samples requires approximately 10 hours, which is longer than the standard 8-hour shift.



P1 - feeds sample or rinse to mixing tee 1

P0 - feeds sample and internal standard to mixing tee 2 and drains spray chamber

Figure 1. Configuration for standard high-throughput application.

Based on previous designs of segmented and continuous flow techniques used at MRI in the past, a customized application (Figure 2) was developed which significantly reduced the time required to rinse the sample in and out of the ICP-MS system. This approach, termed stream-selection, reduces the overall cycle time by eliminating the delay associated with the nebulizer pump, with one major difference from the standard high-throughput approach: a switching valve is required. Like the standard high-throughput application, liquid handling may be performed using one ISIS pump in combination with the on-board nebulizer pump. The preferred configuration does away with the standard nebulizer pump entirely and uses two ISIS pumps for liquid handling.

In this configuration, the sample and rinse streams are independent and the ISIS valve selects which stream goes to the nebulizer. In addition, the flow rate of the sample stream is not coupled to the nebulizer and can be adjusted without disturbing the plasma. With this design, one ISIS pump (Figure 2, P1) is used to feed rinse solution to the nebulizer and add the internal standard. The other ISIS pump (Figure 2, P2) is used to manage the sample. During the load step, the sample is transferred at the maximum uptake rate to the valve. The pump is then slowed to the analysis speed and after a short delay (3 to 5 seconds) to allow the tubing to relax, the sample flow is switched online to the internal standard mixing tee and nebulizer. This arrangement maintains the advantages of constant-flow nebulization, with two additional benefits: the transfer time of the sample to the spray chamber is minimal since there is no pump between the valve and the nebulizer, and rinsing of the spray chamber can begin immediately upon completion of data acquisition by switching the valve back to the load position.

Using this system, a stable signal can be attained in approximately 20 seconds after the autosampler probe enters a sample, and rinse out from 1,000 µg/L to < 1 µg/L can still be accomplished within ~20 seconds of the completion of data acquisition. With a 40-second read time, the total time required for a single sample is reduced from approximately 120 seconds to approximately 70 seconds (rinse in/stabilize, 20 seconds; data acquisition, 40 seconds; and rinse out, 10 seconds). Note that the programmed rinse time is only 10 seconds. Since rinsing of the spray chamber continues to occur during the 20-second load step

for the following sample, the effective rinse time is actually 30 seconds. In certain circumstances (for example, samples of similar matrix composition with moderate analyte levels), the programmed rinse time could be eliminated altogether, reducing the cycle time even further. Using the CETAC ASX-510 autosampler, a fully loaded tray of 270 samples (three racks with 90 samples each) with calibration and QC checks every 20 samples requires approximately 6 hours, an improvement of approximately 40%. More significantly, the analysis can be completed in a single shift, with time available for a second run to be prepared and set up for after-hours analysis. A typical work day using this configuration is shown in Table 2, and a total of 540 samples can be processed daily.

Table 2. Typical Work Schedule with the Stream Selection Application

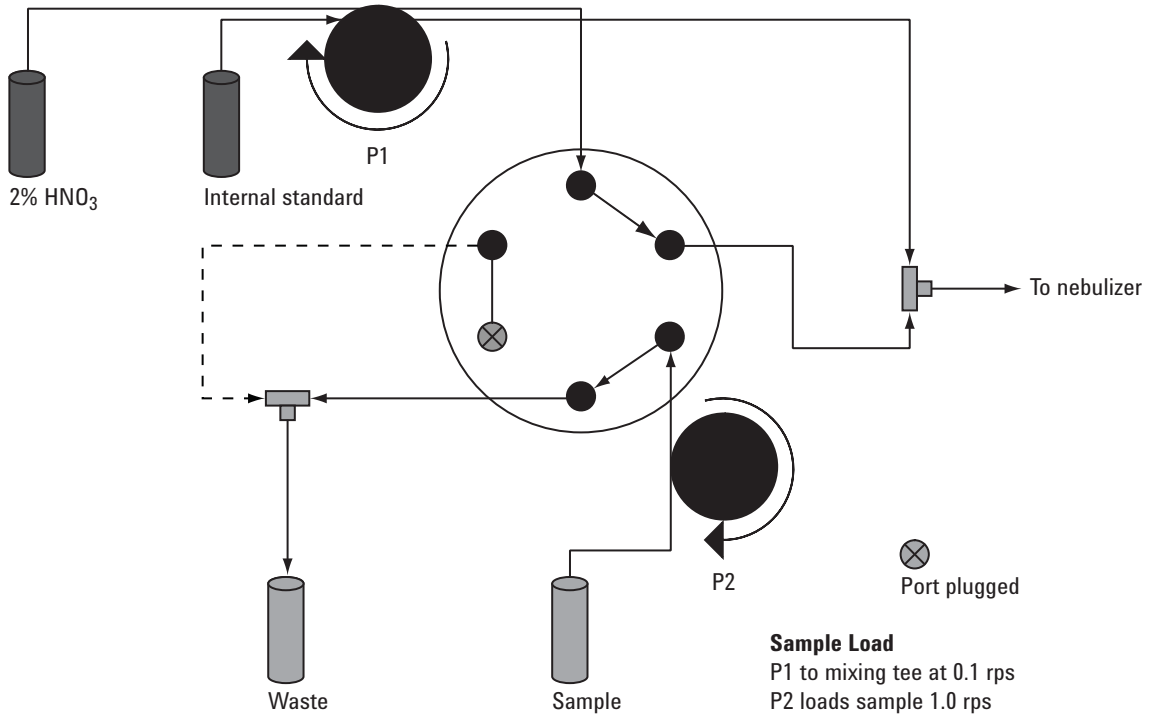
Time	Activity
8:00 - 8:30 a.m.	Instrument maintenance - check cones, pump tubing, and torch. Replace if necessary
8:30 - 9:15 a.m.	Plasma ignition and warm-up, load samples, setup software,download results from previous run
9:15 - 9:30 a.m.	Tuning and performance check
9:30 a.m.	Start run #1 (270 samples)
10 a.m. - 2:30 p.m.	Sample preparation for second run
3:30 p.m.	First run complete
3:30 - 4:00 p.m.	Instrument maintenance - check cones, pump tubing, and torch
4:00 - 4:30 p.m.	Plasma ignition and warm-up, load samples, set up software
4:30 - 4:45 p.m.	Tuning and performance check
4:45 p.m.	Start run #2 (270 samples)
10:45 p.m.	Run complete, instrument to standby

Results and Discussion

SRM Results

NIST 1643e was read 72 times over the course of the study. A control chart for six elements, selected to cover the full range of concentrations and shown with target recovery limits of ± 30%, is presented in Figure 3. Actual recoveries and %RSDs are presented in Table 3. Note that measured concentrations were actually 10 times lower than the certificate value and these results are corrected for dilution.

2A - Sample Load



2B - Sample Inject

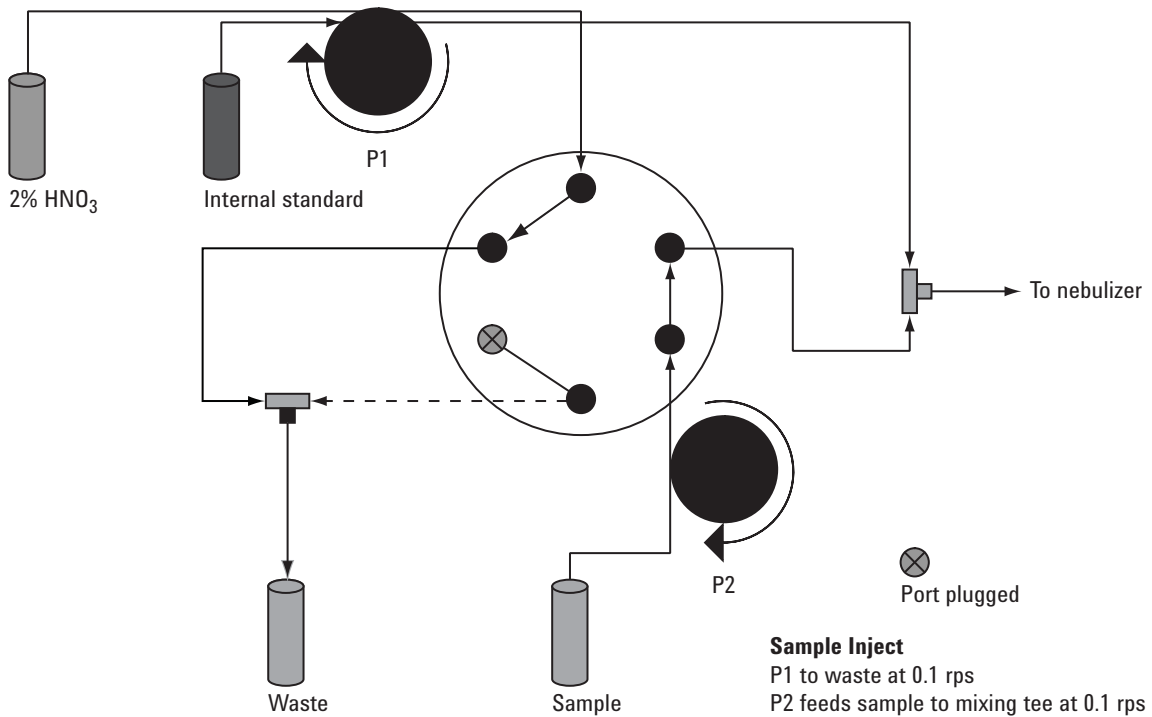


Figure 2. Configuration for stream selection application.

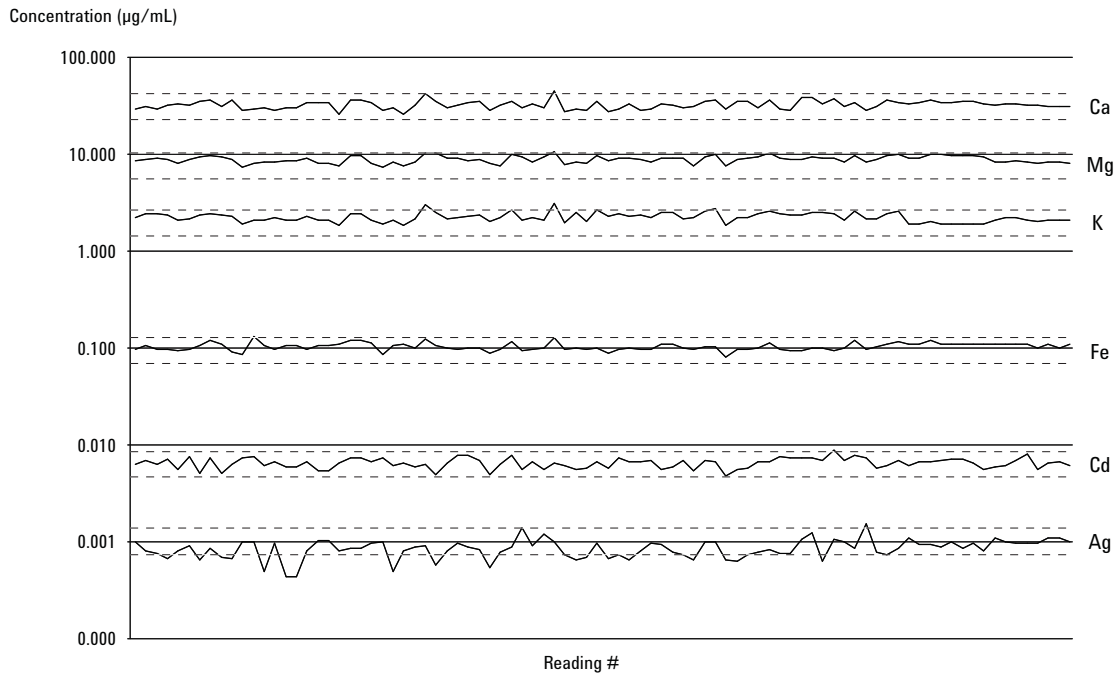


Figure 3. Long-term stability of six representative elements in NIST 1643e (diluted 10x) covering the range of concentrations.

Table 3. Recovery of Certified Concentrations in NIST 1643e, n = 72

Element	Expected (mg/L)	Actual (mg/L)	%RSD (n = 72)	Recovery (%)
Be	0.014	0.014	19	98.5
Na	20.74	22.09	11	107
Mg	8.037	8.867	8.5	110
Al	0.142	0.148	25	105
K	2.034	2.246	11	110
Ca	32.30	32.54	10	100
V	0.038	0.039	8.9	103
Cr	0.020	0.021	11	106
Mn	0.039	0.041	8.4	105
Fe	0.098	0.104	9.0	106
Co	0.027	0.027	7.7	101
Ni	0.062	0.063	10	101
Cu	0.023	0.022	15	94.1
Zn	0.079	0.079	12	101
As	0.060	0.064	12	106
Rb	0.014	0.013	16	92.2
Sr	0.323	0.312	6.4	96.6
Mo	0.121	0.118	7.7	97.4
Ag	0.001	0.001	22	81.4
Cd	0.007	0.007	12	99.3
Sb	0.058	0.056	10	96.3
Ba	0.544	0.516	15	94.9
Tl	0.007	0.007	25	94.5
Pb	0.020	0.018	19	88.6

Sample Results

Samples were analyzed without incident for the duration of the project. Using this approach, 2,500 samples were analyzed for dissolved and soluble element composition (a total of 5,000 analyses) in approximately 10 days. Analytical results were exported to a dedicated database using post-run macros for statistical analysis.

As expected, the elemental distribution in most samples was dominated by the mineral elements, with Na, K, Ca, and Mg accounting for > 98% of the total elemental composition. Elements typically associated with urban airborne particulates, such as aluminum, iron, and zinc, were found in moderate (> 0.5 mg/L) to high (> 1 mg/L) concentrations in all samples. This was expected since sampling took place primarily in urban areas.

In all cases, measured concentrations were higher in the extractable analysis compared to the dissolved analysis. This was expected since particulate matter in the sample was expected to release loosely bound elemental components to the extracting solvent. Several samples were found to contain levels of toxic metals at least 10 times higher than the average value, but no conclusions can be made since site-specific information was not provided.

Conclusions

It has been demonstrated that with careful selection of the collection fluid, samples collected by the SpinCon advanced air sampler are directly compatible with trace element analysis. By using semiquant analysis in He-only mode, with custom ISIS programming to maximize throughput, it was possible to analyze 2,500 samples for dissolved and extractable elemental composition in approximately 2 weeks, meeting the project turnaround time requirements. This ISIS program could also be used to improve throughput in quantitative applications with similar results. The performance of the Agilent 7500c system was stable and reliable for the duration of the project as demonstrated by good recoveries for the NIST 1643e water CRM. The use of macros to download and export sample results significantly reduced the time spent preparing analysis reports and produced data in a format easily imported by our statistical analysis software.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

The information contained in this publication is intended for research use only and is not to be followed as a diagnostic procedure.

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc. 2007

Printed in the USA
January 30, 2007
5989-6123EN

