

Using ion chromatography with electrospray ionization mass spectrometry for the determination of cations and amines in alkanolamine scrubbing solutions

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Keywords

HPIC, Integrion, Dionex IonPac CS19-4 μ m column, ISQ EC mass spectrometer, single quadrupole mass spectrometer, Dionex CERS 500e suppressor, inorganic cations, IC-MS, ESI

Goal

To confirm identities of μ g/L to mg/L concentrations of ammonium, calcium, and alkylamines in high mg/L concentrations of alkanolamines by IC-ESI MS

Introduction

Natural gas (methane) is an important energy resource, accounting for 21.6% of the total energy consumed in 2015, and is primarily used for heating, cooking, vehicle fuel, raw materials for various chemicals and plastics production, and to generate electricity.¹ As a result of hydraulic fracturing of previously inaccessible shale deposits, the United States has moved from a moderate producer to the highest producer of natural gas, followed by Russia, Iran, Canada, and Qatar.¹ However, many of the wells that use hydraulic fracturing contain sour gas, which contains undesirably high concentrations of hydrogen sulfide (H_2S) (>5.7 mg/m³) and high concentrations of carbon dioxide (CO_2) gas.² Sour crude natural gas is very acidic, toxic, and highly corrosive, requiring treatment with amine-rich scrubber solutions to neutralize the CO_2 and remove the H_2S gas impurities.^{3,4}

The scrubbing amine process typically uses alkanolamines, such as methyldiethanolamine (MDEA), diethanolamine (DEA), and ethanolamine (EA), to neutralize the sour gas impurities. When the neutralizing capacity is deemed inefficient, the amine solutions are regenerated and stripped of elemental sulfur. Dissolved salts (heat stable amine salts) remain, building up over time resulting in higher maintenance costs, and higher incidents of corrosion.⁵ Determinations of both the amine concentrations and the heat stable amine salts are needed to ensure a pure product and an efficient scrubbing process. These determinations can be challenging in the concentrated scrubbing amines solution.

For the determination of ionic components, ion chromatography (IC) with suppressed conductivity detection is the analytical method of choice as previously demonstrated for anion and organic acid determinations in heat stable amine salt solutions.^{6,7} Cation determinations at $\mu\text{g/L}$ concentrations in a more concentrated scrubbing amine solution can be demanding. Therefore, a low mass confirmatory detection method, such as a mass spectrometry (MS) optimized for low mass, is needed to provide molecular and structural information. In MS detection, gaseous ionic species are separated by mass/charge (m/z), thereby providing molecular specificity, selectivity, and confirmatory information.

Combining IC with MS takes advantage of the strengths of both techniques. Cation exchange chromatography when combined with eluent generation and suppressed conductivity detection provides chromatographic selectivity, analytes in the ionic form, and compatibility with the MS. Electrospray ionization (ESI) is used to introduce the liquid IC stream as a fine spray into the MS source. The HESI-II probe improves the ESI interface by allowing the use of high temperatures and voltage to deliver better desolvation and enhanced sensitivity; as a result, make-up solvent is not needed.

In this application note, separations of $\mu\text{g/L}$ to mg/L concentrations of ammonium, calcium, and alkylamines in high concentrations of (mg/L to percent) alkanolamines are demonstrated on the Thermo Scientific™ Dionex™ IonPac™ CS19-4 μm (2 × 250 mm) column. The MDEA, DEA, and EA scrubbing matrix is also determined from the 1000-fold diluted samples. The ions elute within 35 min using an electrolytically generated methanesulfonic acid (MSA) gradient from 4 to 65 mM. The ions are detected serially by suppressed conductivity and MS in full scan and selected ion monitoring (SIM) modes without the aid of a desolvation solvent. This IC-MS application is executed on the Thermo Scientific™ Dionex™ Integrion™ HPIC™ ion chromatography system and the Thermo Scientific™ ISQ™ EC single quadrupole mass spectrometer.

Experimental

Ion chromatography

- Thermo Scientific™ Dionex™ Integrion™ HPIC™ system, Reagent-Free™ IC (RFIC™) model with a second 6-port injection valve (P/N 22153-62027) used as a diverter valve and CD Conductivity Detector
- Thermo Scientific™ Dionex™ AS-AP autosampler
- Thermo Scientific™ Dionex™ AXP-MS auxiliary pump (P/N 060684) to supply external water for the suppressor
- IC-MS Installation Kit, P/N 22153-62049

Mass spectrometry

- Thermo Scientific™ ISQ EC™ single quadrupole mass spectrometer
- Thermo Scientific syringe pump (P/N 1245740) for method optimization
- Thermo Scientific™ HESI-II probe

Software

Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, 7.2.6

Table 1 lists the consumable products recommended for the Dionex Integrion RFIC HPIC system configured for suppressed conductivity and MS detections.

Table 1. Consumables list for the Dionex Integrion HPIC system

Product Name	Description	Part Number
Thermo Scientific™ Dionex™ IC PEEK Viper™ fitting tubing assembly kits	Dionex IC Viper fitting assembly kit for the Integrion system configured for eluent generation and conductivity detection: Includes one each of P/Ns: 088815–088821	088798
Dionex AS-AP Autosampler items	Vial Kit, 10 mL Polystyrene with Caps and Blue Septa, 100 each	074228
	Vial Kit, 1.5 mL Polypropylene with Caps and Septa, 100 each	079812
	2.5 µL injection sample loop, prepare 7.7 in length (197 mm) of red PEEK tubing (0.005 in, 0.127 mm i.d.)	--
Thermo Scientific™ Dionex™ EGC™ 500 MSA Eluent Generator cartridge	Eluent generator cartridge recommended for this application	075779
Thermo Scientific™ Dionex™ CR-CTC™ 600 Electrolytic trap column	Continuously regenerated trap column used with Dionex EGC MSA 500 cartridge and required for Integrion system	088663
Thermo Scientific™ Dionex™ HP Degasser module	Degasser installed after Dionex CR-TC trap column and before the injection valve. Used with eluent generation— included with Integrion RFIC model	075522
Thermo Scientific™ Dionex™ CERS™ 500e suppressor	Recommended suppressor for 2 mm i.d. columns when the suppressor is in external water mode	302664
Thermo Scientific™ Dionex™ IonPac™ CG19-4µm column	Cation guard column, 2 × 50 mm	078839
Dionex IonPac CS19-4µm column	Cation separation column, 2 × 250 mm	078836
IC-MS Installation Kit	IC-MS Installation Kit includes tubing, mixing tee, and Dionex SRD 10 device	22153-62049
Syringe filters	Syringe filters suitable for IC, 0.45 µm, PES	Fisher Scientific 725-2545
Thermo Scientific™ Nalgene™ Rapid Flow Sterile Disposable Filter Units, PES membrane	Used for vacuum degassing of ASTM® Type I DI water	Fisher Scientific 09-741-03

IC-MS conditions		IC-MS conditions (continued)	
Columns:	Dionex IonPac CG19-4 μ m guard, 2 \times 50 mm Dionex IonPac CS19-4 μ m separation 2 \times 250 mm	Run Time:	35 min
Eluent:	4 mM MSA (0 to 0.1 min), 4 to 60 mM (0.1 to 27.5 min), 4 mM (27.6 to 35 min)	Background Conductance:	< 1 μ S/cm
Eluent Source:	Dionex EGC 500 MSA eluent cartridge, Dionex CR-CTC 600 trap column and high-pressure degas module	Noise:	< 1 nS/cm
Flow Rate:	0.25 mL/min	System Backpressure:	~2200 psi
Column Temp.:	30 $^{\circ}$ C	MS Detection:	+ESI, +3000 V, full scan, 18–250 m/z
Detection/ Suppressor Compartment:	15 $^{\circ}$ C	Flow (N_2):	Sheath: 50 psi, Aux: 4 psi; Sweep: 0.2 psi
Detection:	Suppressed conductivity, Dionex CERS 500e suppressor, 48 mA, 2 mm, external water mode (driven by AXP-MS pump at 0.5 mL/min)	Temperatures:	Vaporizer (Ionization): 250 $^{\circ}$ C; Ion Transfer: 250 $^{\circ}$ C
		Chromatography Width:	10 points at 15 s
		Desolvation Solution:	None
		SIM Filter:	1 AMU
		CID (V):	Table 2

Table 2. Analyte and SIM table

Analyte	Formula	Isotopic (Accurate) Mass	Ion m/z	CID (V)
Ammonium as NH_4^+	NH_4^+	18.031	18	10
Ammonium as $NH_4^+ \cdot H_2O$	$NH_4^+ \cdot H_2O$	36.045	36	5
Calcium as $Ca^+ \cdot 2H_2O$	$Ca^+ \cdot 2H_2O$	75.985	76	10
Dibutylamine	$C_8H_{19}N$	129.152	130	10
Diethanolamine (DEA)	$C_4H_{11}NO_2$	105.079	106	20
Diethylamine	$C_4H_{11}N$	73.089	74	15
Dimethylamine	C_2H_7N	45.058	46	10
2-Dimethylaminoethanol	$C_4H_{11}NO$	89.084	90	20
Ethanolamine (EA)	C_2H_7NO	61.053	62	15
Ethylamine	C_2H_7N	45.058	46	10
Hydrazine	N_2H_4	32.037	33	10
Magnesium	Mg	23.985	24	10
Magnesium as $2Mg^+ \cdot H_2O$	$2Mg^+ \cdot H_2O$	65.981	66	10
Methylamine	CH_5N	31.042	32	10
Methylaminoethanol	C_3H_9NO	75.068	76	10
Methyldiethanolamine (MDEA)	$C_5H_{13}O_2N$	119.095	120	10
Potassium	K	38.964	39	10
Sodium as Na	Na	22.990	23	10
Sodium as $Na^+ \cdot 2H_2O$	$Na^+ \cdot 2H_2O$	59.011	59	10
Triethanolamine (TEA)	$C_6H_{15}NO_3$	149.105	150	25

Note: The optimum settings and responses may vary on different instruments; thus, optimization of ISQ EC MS local source conditions and acquisition parameters is highly recommended for best results.

Reagents and standards

- ASTM Type 1 deionized water⁸ (DI), degassed by ultrasonic agitation with applied vacuum
- Thermo Scientific™ Dionex™ Combined Six Cation Standard II, P/N 046070
- Thermo Fisher™ acetonitrile, HPLC grade, P/N A998. Used for offline conditioning of the column during installation.
- Thermo Scientific™ Dionex™ CS12A Eluent Concentrate solution (400 mM Methanesulfonic acid (MSA)) P/N 057562. Used for offline conditioning of the column during installation.

Thermo Fisher™, ACS Certified grade:

- Sodium chloride, crystalline, S271-500
- Potassium chloride, crystalline, P217-500
- Ammonium chloride, crystalline, A661-500 or Ammonium hydroxide, w = 28–30%, A669-500
- Calcium chloride dihydrate, crystalline, C79-500
- Magnesium chloride, hexahydrate, crystalline, M33-500

Sigma-Aldrich®, ACS Reagent grade:

- Dibutylamine, P/N 471232-100mL
- Diethanolamine, crystalline, P/N D8885-500mL
- Dimethylamine, anhydrous, P/N 295280
- 2-Dimethylaminoethanol, P/N 471453-100mL
- Ethylamine, anhydrous, P/N 301264
- Hydrazine, w = 98% anhydrous, P/N 215155-50G
- Monoethanolamine, P/N 411000-100mL
- Methylmonoethanolamine, P/N 471445-25mL
- Methyl-diethanolamine, P/N 471825-250mL
- Triethanolamine, P/N 90279
- Methylamine solution, w = 40% in water, Sigma-Aldrich P/N 426466-100 mL

Standard and sample preparation

Prepare degassed ASTM Type I water by applying vacuum filtration with ultrasonic agitation to remove the dissolved gases.

For convenience, working and MDL standards were prepared by serial dilutions of the Dionex Six Combined Cation II Standard solution (50 mg/L lithium, 200 mg/L sodium, 250 mg/L ammonium and magnesium, and 500 mg/L potassium and calcium) with DI water (100,000-, 50,000-, 10,000-, 5000-, 1000-, 500-, 100-, and 50-fold). The final concentrations of the working standards ranged from 0.025 to 25 mg/L for ammonium and magnesium, 0.020 to 20 mg/L sodium, 0.005 to 50 mg/L for potassium, and 0.10 to 50 mg/L for calcium.

Alternatively, stock standards can be prepared by adding the reagent (shown in Table 3) to a 100 mL HDPP bottle, adding 100 g of DI water, capping the bottle, and shaking until the reagent is fully dissolved. Label and store at 20 °C.

Prepare a 10 mg/L combined intermediate standard by adding 1 g of each 1000 mg/L individual stock standard to a 100 mL HDPP bottle. Add DI water to a final weight of 100.00 g. Cap the bottle and invert to mix. Store the standard at 20 °C until it is needed.

To prepare the combined EA, DEA, and MDEA working standards, dilute the 10,000 mg/L individual stock standards with DI water to 3333, 2000, 1000, 500, 200 mg/L combined standards.

Standards for MS optimization experiments

For the MS optimization experiments, infuse individual 10 mg/L standards with and without eluent. Prepare these standards by diluting 200 µL of the 1000 mg/L standard with DI water to 20 g total weight. For the IC-MS optimization experiments, prepare the 10 mg/L ammonium and sodium, 1000-fold diluted DEA standard by diluting 20 mg of DEA reagent and 200 µL of the 1000 mg/L ammonium and sodium standards with DI water to 20 g total weight.

Table 3. Amount of reagent needed to prepare 100 mL of 1000 mg/L individual stock standards

Analyte: Reagent	FW (g/mol) (Density, g/mL) ¹⁰	Reagent (mg)	DI water (g)
Ammonium: Ammonium chloride	53.489	297	100.00
Ammonium: Ammonium hydroxide (w = 29%)	35.04 (0.90)	345	99.89
Calcium: Calcium chloride, dihydrate	147.01	368	100.00
Dibutylamine	129.247 (0.76)	100	99.87
DEA	105.137	1000 ⁺⁺	98.77
Diethylamine	73.139 (0.71)	100	99.86
Dimethylamine	45.085 (0.67)	100	99.85
2-Dimethylaminoethanol	89.138 (0.89)	100	99.89
Ethanolamine	45.085 (0.81)	1000 ⁺⁺	99.88
Ethylamine	45.085 (0.67)	100	99.85
Hydrazine	32.046 (1.01)	100	100.00
Magnesium: Magnesium chloride, hexahydrate	203.29	847	100.00
Methylamine, w = 40%	31.058	250	99.75
Methylaminoethanol	75.111 (0.93)	100	99.90
MDEA	119.164 (1.04)	1000 ⁺⁺	99.04
Potassium chloride	74.548	191	100.00
Sodium: Sodium chloride	58.44	254	100.00
TEA	149.19 (1.1)	100	99.91

¹⁰Density values were obtained from PubChem®.

⁺⁺The final concentration was 10,000 mg/L for the stock standard

MSA-acetonitrile solutions for offline conditioning of the Dionex IonPac CS19-4 μ m columns

If a gradient offline pump is available, prepare three solutions.

- Eluent A: 200 mL degassed Type I DI water.
- Eluent B: Prepare 200 mL of 80 mM MSA by diluting 40 mL of the Dionex CS12A Eluent Concentrate solution in 160 mL of degassed DI water.
- Eluent C: Prepare 200 mL of 95% acetonitrile by diluting 190 mL of acetonitrile with 10 mL of degassed DI water.

Separately mix the Eluent B and C solutions by inverting the sealed containers several times. Connect the containers of degassed DI water, 80 mM MSA solution, and 95% acetonitrile solution to Eluent A, Eluent B, and Eluent C, respectively. Prime the three eluent lines.

For isocratic offline conditioning of the Dionex IonPac CS19-4 μ m column, prepare 200 mL of 8 mM MSA by diluting 4 mL of Dionex CS12A Eluent Concentrate solution in 196 mL DI water. Prepare 200 mL of 8 mM MSA 10% acetonitrile solution in DI water by adding 4 mL of Dionex CS12A Eluent Concentrate solution and 20 mL of acetonitrile to 176 mL of degassed Type I DI water. Mix each solution thoroughly by inverting the sealed container several times. Connect the 8 mM MSA container to the pump and prime the pump.

Sample preparation

Dilute the alkanolamine scrubbing solution samples 1000-fold prior to analysis. Filter samples (0.45 μ m, nylon) if particulates are observed.

Instrument Setup

Plumbing the Dionex Integrion HPIC system and ISQ EC Single Quadrupole mass spectrometer

The Integrion HPIC system is plumbed as a Reagent-Free IC (RFIC) system using eluent generation with the suppressor in external water mode supplied by the Dionex AXP-MS auxiliary pump. Additionally, IC-MS applications use a second 6-port IC injection valve as a diverter valve and a Dionex SRD-10 Suppressor Regenerant Device to monitor the flow of suppressor regenerant. The second valve is placed between the IC and the MS to divert sample matrix to waste.

The Dionex SRD-10 device is placed between the Regen Out port of the suppressor and the Regen In port of the Dionex CR-CTC trap column. The Dionex SRD-10 device triggers the Integrion pump to turn off when an air bubble is detected for a considerable time instead of the regenerant flow, thereby preventing un-neutralized acid directed to the MS. In this application, the Dionex SRD-10 device was triggered ~ 5 min after the regenerant flow stopped. Install and plumb the IC-MS system according to Figure 1.¹¹ Detailed instructions are described in Thermo Fisher Scientific technical notes 175⁹ and 72611¹¹, the instrument operating manuals, and MS maintenance videos.¹²⁻¹⁴

Conditioning electrolytic devices and columns

Do not remove consumable tracking tags on the columns and consumable devices. These tags are required for consumables monitoring functionality.

Condition the Dionex EGC 500 MSA cartridge and Dionex CR-CTC 600 trap column according to the Consumables Installation instructions on the Chromeleon Instrument panel for the Integrion IC system. Hydrate and condition the Dionex CERS 500e 2 mm suppressor according to the suppressor manual instructions.¹⁶

Offline conditioning of the Dionex IonPac CS19-4 μ m columns

The Dionex IonPac CS19-4 μ m column requires an offline conditioning process prior to use. Acetonitrile can damage some of the devices so do not pump the acetonitrile solution through the eluent generator cartridge, the trap column, or suppressor. Note that the recommended column oven temperatures are from 15 to 30 °C.

If a gradient pump is available, condition the Dionex IonPac CG19-4 μ m guard and Dionex IonPac CS19-4 μ m separation columns offline at 0.13 mL/min while directing the flow to waste (Table 4).

Table 4. Quick Start procedure using a gradient pump at 0.13 mL/min¹⁵

Time (min)	MSA (mM)	Acetonitrile (%)
0 to 5	8	0
5 to 10	8	0 to 9.5
10 to 60	8	9.5
60 to 65	8	9.5 to 0

If a gradient pump is not available, use the Dionex AXP or other isocratic offline pump to condition the columns at 0.13 mL/min (Table 5) while directing the flow to waste. Prime the pump with each new solution.

After conditioning the columns, remove them from the offline pump, and re-install them in the Integrion RFIC column oven. Flush the offline pump with DI water to remove residual acid and acetonitrile solutions.

Table 5. Quick Start procedure using an isocratic pump at 0.13 mL/min¹⁵

Time (min)	MSA (mM)	Acetonitrile (%)
0 to 5	8	0
5 to 65	8	9.5
65 to 75	8	0

Configure the IC-MS modules in the Chromeleon CDS software according to TN175 and TN72611. The Chromeleon CDS configuration parameters are summarized in Table 6. The method was developed using the “Easy” mode by selecting parameters one step below default on robustness and stable analyte and one step above default on mobile phase using the Chromeleon Instrument Method Wizard program (Figure 2). These values were translated into the “Advanced” mode to show the CID and sampling rate parameters. Additionally, to further optimize this method, the MS was infused with 10 mg/L single analyte standards while teeing in the suppressed eluent stream.

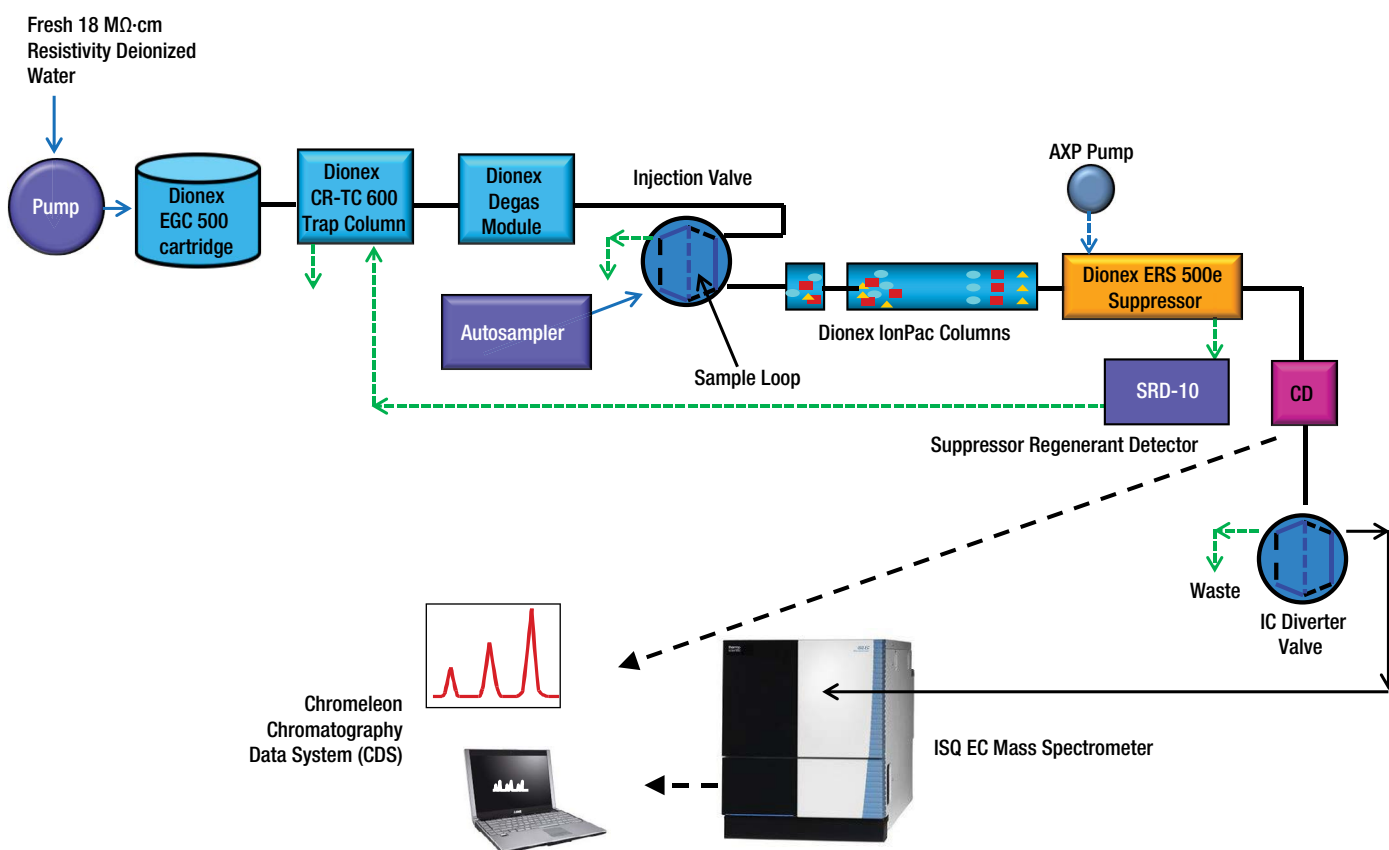


Figure 1. Flow diagram for IC-MS

Table 6. Summary of system configuration for the high-pressure Dionex Integriion HPIC system, Integriion RFIC model

Tab	Action	Result
Dionex Integriion HPIC Module		IC System
General	Link to USB address	
Pump	--	Flow rate and pressure limitations are displayed
Detectors	--	Automatically detected
Electrolytics	--	Automatically detects Dionex eluent generator cartridge, and Dionex CR-CTC 600 trap column, suppressor
Inject Device	Click boxes Inject Valve and HP_Valve	Activates both valves for use with IC-MS applications. The HP_Valve is used as a diverter valve between the IC and MS instruments.
	Double left-click on InjectValve	Opens the device configuration information on the injection valve on the injection valve
	Select Autosampler HP_Valve	Assigns control of the injection valve to the autosampler Used as a diverter valve
Thermal Controls	--	Automatically detects thermal control options for column, detector, and suppressor
TTL Inputs	Double left-click on <i>TTL_Input_1</i>	Selecting TTL Input 1
	Select <i>Inverted Mode</i>	Directs the TTL connected device (Integriion pump) to turn off when regenerant flow is off for 5 min
	Click box of <i>Pump On</i>	Connects to Pump
Options	--	Automatically detects Pump Degasser and Seal Wash pump
Pump Wellness Module		Monitors and allows display of Integriion pump pressure
Devices	Click pressure signal box	Activates pressure monitoring feature
Add Dionex AS-AP Autosampler		Delivers sample to IC injection valve
Add module	Link to USB address	
Sharing	--	Only if more than one instrument is detected. If this option is present, select the instrument used for this application
Segments / Pump Link	--	Select 10 mL polystyrene vials or 1.5 mL vials for "Red", "Blue", and "Green" sections
Options	Injection Mode	Select Push
	Autosampler Valves	If valves are present, assign function. Not used in this application
	Select Buffer Size	1200 µL
	Select Syringe Size	250 µL
	Loop Size	Enter Injection Loop size (2.5 µL)
	Temperature Control box	Click on box to activate temperature control. Set temperature range
Add Dionex Auxiliary Pump Module		Pumps water through suppressor regenerant channel
General	Select COM3 or COM5	Connects communication from auxiliary pump to configuration
Pump Type	Select type of pump	AXP or AXP-MS pump
Add Thermo Scientific ISQ EC Mass Spectrometer		Mass spectrometer module
Add module	Select "Mass Spectrometry", ISQ EC IC-MS"	Selects the correct module
General	Deselect Hardware inject synchronization	Do not select. Chromeleon controls injection
	Select ActiveLow for Remote Start	Setting for Dionex AS-AP autosampler
Finish Instrument Configuration		Check, save, and close
Check Configuration	Select Controller	(On the top banner above the icons.)
	Select Check Configuration	Checks the configuration and reports errors
	Save and close	Saves and closes the configuration program. Updates the IC and MS instruments as to the changes made in the configuration program

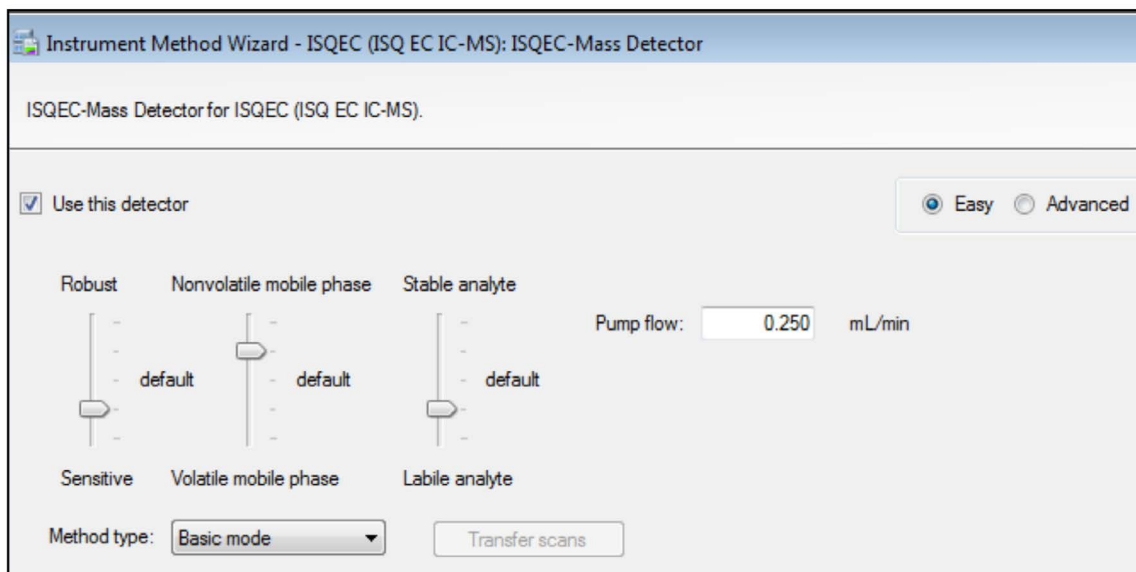


Figure 2. Using the Instrument Method Wizard to Select MS starting conditions

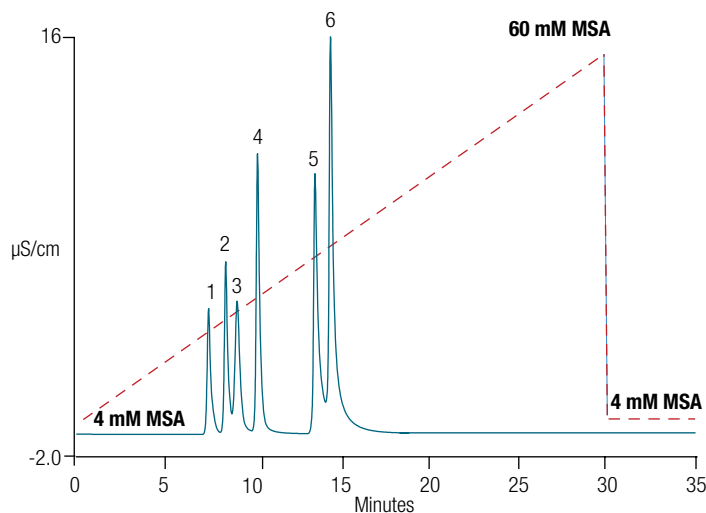
Optimizing the MS

MS optimization was conducted three ways to obtain and ensure the optimum conditions: 1) infusion of individual 10 mg/L standards using a syringe pump, 2) infusion of individual 10 mg/L standards blended with the IC eluent flow, and 3) injection of 10 mg/L sodium and ammonium spiked into 1000-fold dilution of DEA standard through the IC-MS. The MS was optimized by varying the CID, temperatures, and gas flows using Real Time Scan mode for the first two experiments. Infusion experiments have the advantages of quickly determining how the ions respond to the conditions, and easy identification of hydrate adducts. In the third optimization, the MS starting conditions were obtained by using the “Easy” mode translated into the “Advanced” instrument method mode with previously determined CID voltages. The optimum responses of the sodium, ammonium, and DEA bare ions and the sodium and ammonium hydrates were evaluated first by varying the vaporizer temperature at 50 °C increments from 200 to 350 °C. The vaporizer temperature exhibiting the best results, 250 °C, was used while varying the ion transfer temperature. The same process was applied with the sheath gas from 20 to 60 psi in 10 psi increments, aux gas from 2 to 10 psi in 2 psi increments, and sweep gas at 0, 0.2, and 0.5 psi. The IC-MS experiments have the advantage of optimizing the whole system with a standard simulating

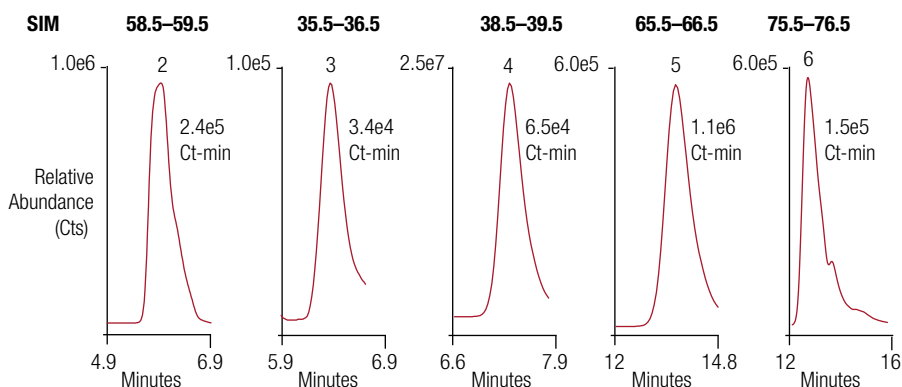
the samples. In summary, the experiments showed that the ammonium hydrate ($\text{NH}_4^+\cdot\text{H}_2\text{O}$) and the sodium hydrate ($\text{Na}^+\cdot 2\text{H}_2\text{O}$) were stable and provided more response than the bare ions, and therefore were used for quantitation. The conditions resulting from these optimization experiments were used in this application note. The IC-MS optimization process is discussed thoroughly in TN72611.¹¹

Results and discussion

In this application $\mu\text{g/L}$ to mg/L concentrations of inorganic cations were determined in 1000-fold diluted alkanolamine samples using a simple acid gradient (4 to 60 mM methanesulfonic acid) at 30 °C and 0.25 mL/min on a 2 × 250 mm Dionex IonPac CS19-4 μm cation-exchange column set (Figure 3). The Dionex IonPac CS19-4 μm column was selected for the preferential selectivity of small polar amines and alkanolamines needed in this application. A 30 °C separation temperature was selected as a compromise between the recommended optimum column temperatures (from 15 to 30 °C) and the operating specifications of the Integrion RFIC system (5 °C above ambient to 80 °C). At column temperatures above 30 °C it was observed that divalent cations had reduced sensitivity by both CD and MS detectors, and increasingly longer retention times.



Columns: Dionex IonPac CG19-4µm, 2 × 50 mm
 Dionex IonPac CS19-4µm, 2 × 250 mm
 MSA Gradient: 4 mM MSA (0–0.1 min),
 4–60 mM (0.1–27.5 min),
 4 mM (27.6–35 min)
 Eluent Source: Dionex EGC-500 MSA cartridge,
 Dionex CR-CTC 600 trap column,
 Dionex high pressure degasser
 Flow Rate: 0.25 mL/min
 Injection Vol.: 2.5 µL
 Column Temp.: 30 °C
 Detector 1: Suppressed conductivity,
 Dionex CERS 500e suppressor,
 48 mA, 30 °C,
 external water mode,
 0.5 mL/min by Dionex AXP-MS pump
 Detector 2: ISQ EC, +ESI, +3000 V source, HESI II
 Scan Mode: Full scan: 18–200 *m/z*, SIM
 Sampling Rate: 15 s chromatography width, 10 points/peak
 Make-up Solvent: None
 Source Temp.: Vaporizer 250 °C, Ion Transfer 250 °C
 N₂ Gas Flow (psi): Sheath 50, Aux 4, Sweep 0.2
 Standard: Dionex Combined Six Cation Standard-II,
 50-fold dilution with DI water



Peaks:	CID (V)	Conc. (mg/L)
1. Lithium	--	1
2. Sodium·2H ₂ O	10	4
3. Ammonium·H ₂ O	5	5
4. Potassium	10	10
5. Magnesium·H ₂ O	10	5
6. Calcium	10	10

Figure 3. Diluted six cation standard

The ions were detected serially by suppressed conductivity and mass spectrometry. Electrospray ionization by the HESI II microprobe was used to introduce the ion flow into the ISQ EC single quadrupole MS where the ions were analyzed in full scan and SIM modes. Sodium (+*m/z* 59), ammonium (+*m/z* 36), magnesium (+*m/z* 66), and calcium (+*m/z* 76) were detected in SIM mode as hydrate adducts with 1 AMU filters to achieve increased sensitivity, whereas potassium and the amines were detected as bare and molecular ions, respectively (Table 3). Due to the new HESI-II interface, no desolvation solvent was needed for this application.

Method development

To assess the validity of the method for the intended application, it was applied to an artificial sample of 100 mg/L sodium and ammonium in 1000-fold diluted MDEA. The alkanolamine matrix ions, such as EA, MDEA, and DEA, were also assayed in the same injection, and as a result a small injection volume (2.5 µL) was selected as a compromise between the demand for sensitivity for the low concentration analytes and to prevent overloading the column and the detectors with the alkanolamines. Alkylamines were detected but not quantified in this application. The experiments (Figure 4) show that sodium, ammonium, and MDEA only needed to be partially resolved chromatographically because they could be fully resolved and detected with the MS. Ethanolamine and triethanolamine were also detected as degradation products of MDEA.

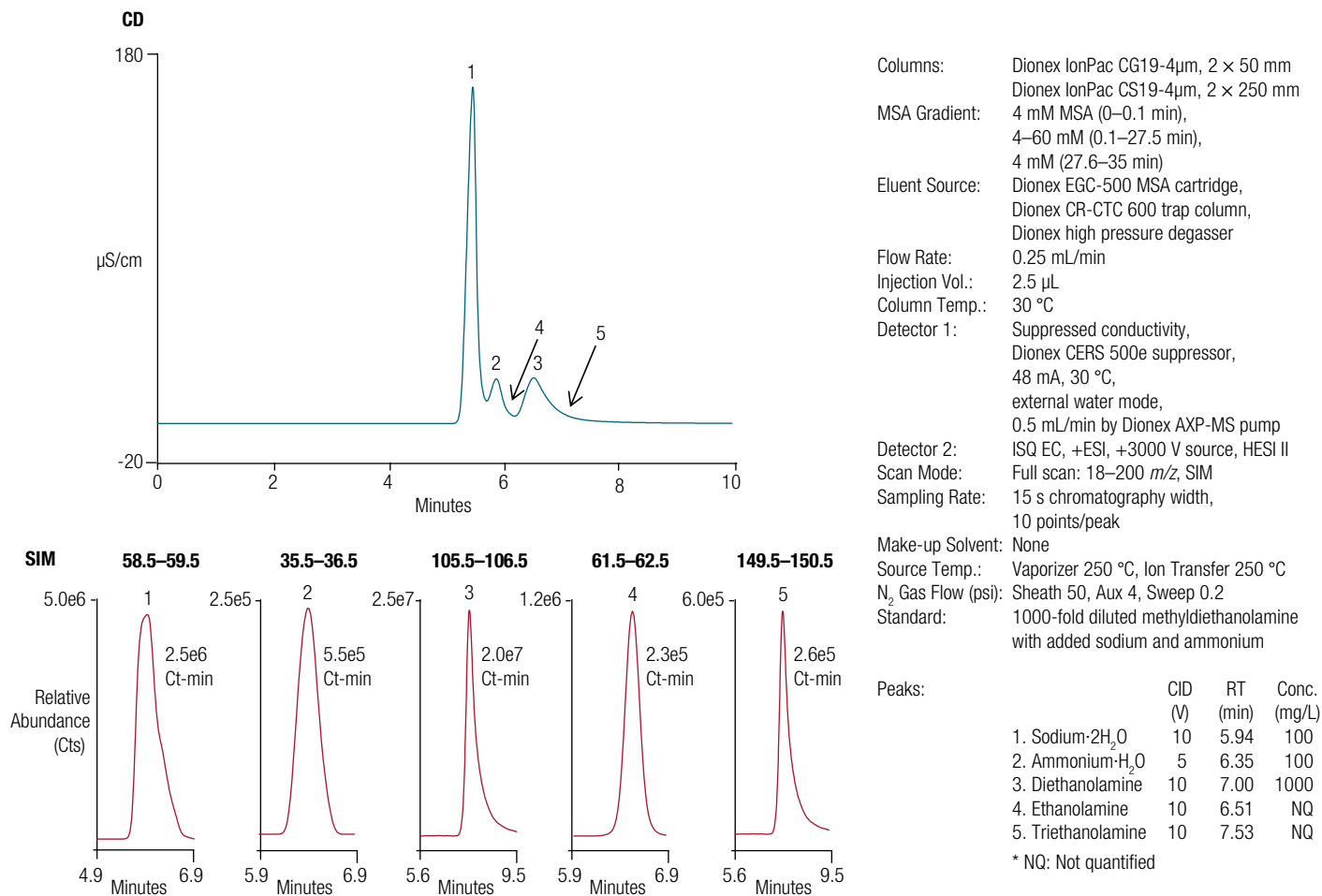


Figure 4. 100 mg/L sodium and ammonium in methyldiethanolamine

Additionally, the MS response to concentration was determined in duplicate for sodium, ammonium, potassium, magnesium, and calcium using 5000-fold to 10-fold dilutions of the Dionex Combined Six Cation II standard (Table 7) to generate the calibration curves. The responses of the alkanolamines were also determined in triplicate from 200 to 3333 mg/L MDEA and DEA, and from 200 to 2000 mg/L EA. Table 5 summarizes the results showing a second order quadratic fit for all ions, with coefficient of determinations (r^2) > 0.99. A 1/x weighting factor was applied for ammonium-water ion for a better fit.

To evaluate sensitivity, the estimated method detection limits (MDL) ($n = 7, 3 \times S/N$) of sodium, ammonium, and magnesium were determined with seven replicate injections of the 10,000-fold diluted Dionex Combined Six Cation II standard solution. The MDLs were determined similarly for potassium and calcium using a 50,000-fold

and 5,000-fold diluted standard, respectively. Low MDLs (< 8 μg/L) were obtained for sodium and potassium, as well as for ammonium (22 μg/L), magnesium (15 μg/L), and calcium (64 μg/L).

Samples

The method was applied to eight samples from refinery scrubbing processes. Figure 5 shows CD and SIM chromatograms of representative scrubbing sample solutions. The 1000-fold diluted EA, DEA, and MDEA samples had low mg/L amounts of sodium, ammonium, and triethanolamine. Methylaminoethanol was also present in the MDEA sample but it was not quantified. EA, DEA, and MDEA were quantified in the diluted samples at concentrations of 2100, 220, and 320 mg/L, respectively. Small amounts of magnesium and calcium, estimated in the μg/L concentrations, were detected by suppressed conductivity. Potassium was not detected by either detector.

Table 7. Summary of calibration and MDL results

Ion	Calibration Range (mg/L)	Type	Coefficient of Determination (r ²)	MDL (µg/L)
Na·2H ₂ O	0.040–20	Quadratic fit, 2 nd order	0.9995	8 ⁺⁺
NH ₄ ·H ₂ O	0.0025–25	Quadratic fit, 2 nd order, weighted 1/x	0.9919	22 ⁺⁺
EA	200–2000	Quadratic fit, 2 nd order	0.9994	ND
DEA	200–3333	Quadratic fit, 2 nd order	0.9971	ND
Potassium	0.005–50	Quadratic fit, 2 nd order	0.9991	4 ⁺⁺⁺
MDEA	200–3333	Quadratic fit, 2 nd order	0.9984	ND
2Mg·H ₂ O	0.025–25	Quadratic fit, 2 nd order	0.9989	15 ⁺⁺
Ca·2H ₂ O	0.050–50	Quadratic fit, 2 nd order	0.9962	64 ⁺⁺⁺⁺

MDL= 3 × S/N, n = 7. ND: not determined. MDL Standard, Dionex Combined Six Cation II standards: ⁺⁺10,000-fold dilution, ⁺⁺⁺50,000-fold dilution, ⁺⁺⁺⁺5,000-fold dilution

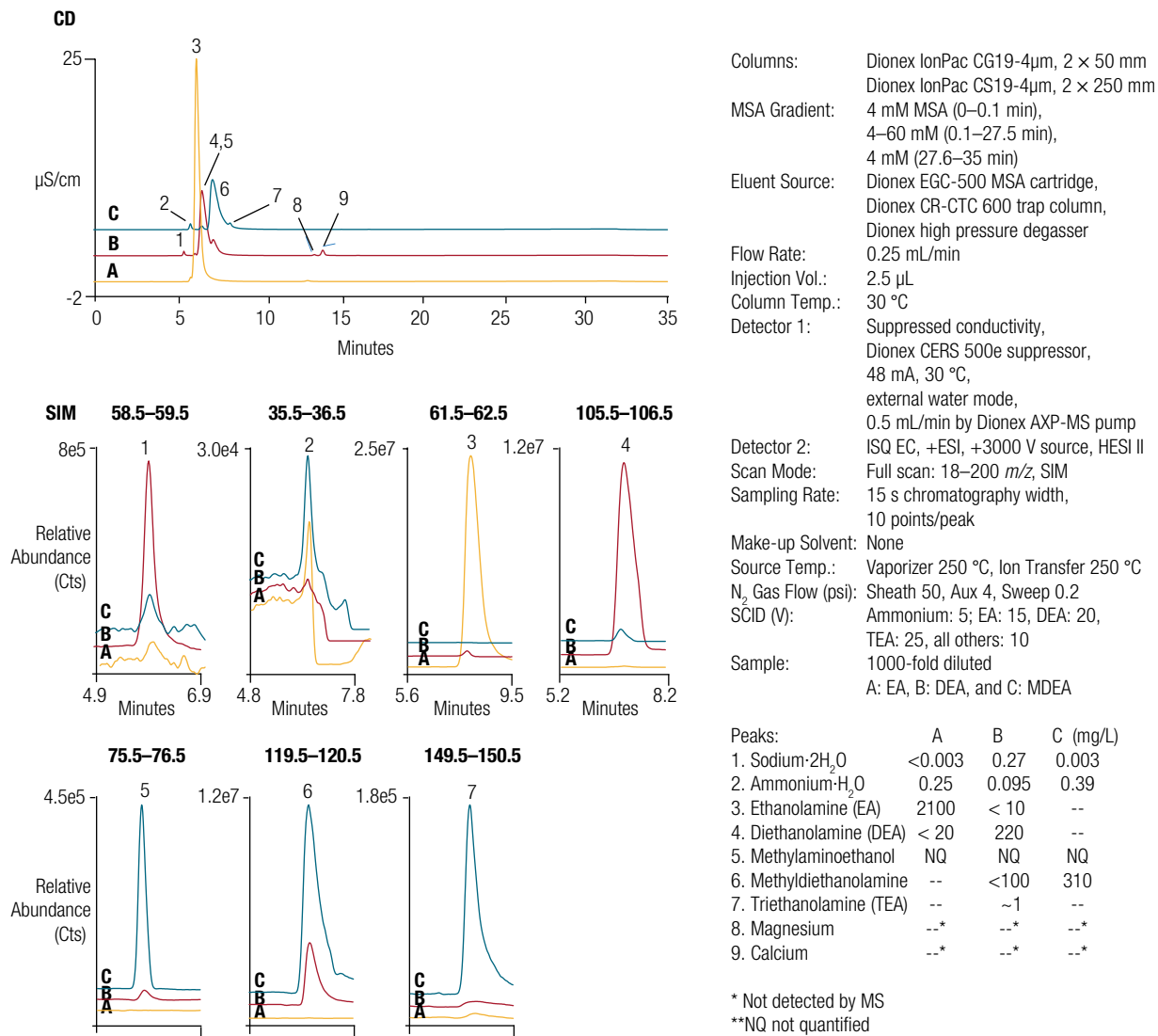


Figure 5. Determinations of amines and cation in 1000-fold dilution of A) EA, B) DEA, and C) MDEA-based scrubbing amine samples

Method accuracy was determined by adding sodium, ammonium, and the main components (amines) to the 1000-fold diluted samples. The recoveries (Table 8) for sodium and ammonium were in the range of 99% to 104%. The recovery values for the matrix components were found in the range of 89% to 101%.

Conclusions

Determinations of alkanolamines and inorganic cations by IC-ESI MS were demonstrated on the Dionex IonPac CS19-4 μ m cation-exchange column using the Dionex Integriion IC and ISQ EC single quadrupole mass spectrometer. The method had good sensitivity for sodium and ammonium hydrate adducts to single digit

μ g/L, despite the small injection volume of 2.5 μ L, while also assaying up to 2000 mg/L of the matrix amine. The method showed good accuracy in EA, DEA, and MDEA as demonstrated by the recovery experiments. IC-MS provided the necessary detection selectivity to ensure an interference-free quantitation of low levels of inorganic cations in the presence of high concentrations of alkanolamines. Through the use of the HESI-II interface no make-up solvent was needed to support the desolvation process, thus reducing the complexity and costs of the analytical approach.

More information can be found in Thermo Fisher Scientific AppsLab Library of Analytical Applications.¹⁷

Table 8. Summary of recovery experiments (n = 3)

Sample	Na ⁺ ·2H ₂ O			NH ₄ ⁺ ·H ₂ O			Matrix		
	Present (mg/L)	Added (mg/L)	Recovery (%)	Present (mg/L)	Added (mg/L)	Recovery (%)	Present (mg/L)	Added (mg/L)	Recovery (%)
EA	--	0.42	99.1	0.25	0.21	101	2100	762	89.4
DEA	0.27	0.96	102	0.095	1.3	104	220	1570	101
MDEA	0.003	0.63	104	0.39	0.93	102	310	971	99.4

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