Determination of N-Nitrosodimethylamine at Part-Per-Trillion Levels in Drinking Waters and Contaminated Groundwaters

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Determination of N-Nitrosodimethylamine at Part-Per-Trillion Levels in Drinking Waters and Contaminated Groundwaters[1]

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Introduction

N-nitrosodimethylamine (NDMA, CAS registry number [62-75-9]) is a highly carcinogenic manufacturing by-product of unsymmetrical dimethyl hydrazine (1,1-dimethylhydrazine), a component of rocket fuel[1]. Prior disposal practices, now strongly discouraged, resulted in the contamination of groundwater near certain military installations with both species. The current regulatory threshold promulgated by the U. S. Environmental Protection Agency (EPA) for NDMA in surface waters designated for drinking is 0.7 ng NDMA/L (0.7 pptr)L[2]. Existing procedures for determining NDMA in aqueous samples typically employ dichloromethane extraction followed by concentration to a final volume of 1 mL, and gas chromatographic analysis of a 2 μL aliquot of concentrate using either a nitrogen-phosphorus detector (NPD)[3,4,5], mass spectrometric detector[6,7,8,9], or chemiluminescent nitrogen detector (CLND)[1,10,11,12,13]. Such a protocol does not permit detection of NDMA at the desired health-based criterion unless high-resolution mass spectrometric (HRMS) detectors are employed[6,14].

The analytical procedure described in this work employed an initial solid-phase extraction of groundwater samples with a preconditioned Empore® C$_{18}$ disk, used to remove interfering neutral species including di-isopropylmethane phosphonate (DIMP), prior to continuous overnight extraction of the filtrate with highest-purity dichloromethane[15]. The dichloromethane extract is concentrated to a final volume of 1 mL; the residues from a 200 μL aliquot of the concentrate are injected onto a gas chromatographic column using a short-path thermal desorber. NDMA is collected at the head of the column near ambient temperature (without cryotrapping), eluted in the conventional manner, and detected using a CLND. The reporting limit for this procedure, 2 ng NDMA/L groundwater, was calculated using two statistically-unbiased procedures[16,17]. The certified range for this procedure is 2 to 40 ng NDMA/L groundwater.

A related procedure permitted unattended analysis of samples for NDMA concentrations exceeding 100 ng NDMA/L groundwater. The sample preparation is the same as that described above; however, 2 μL aliquots of dichloromethane concentrates are injected onto the gas

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chromatographic column using an automatic sampler.

Procedure and Considerations

Analytical procedures capable of achieving the stated regulatory criterion must satisfy numerous challenges, whose nature and their resolution are addressed as follows:

- Not all water supplies are suitable for preparing either standards or spiked samples because small quantities of NDMA, frequently exceeding the regulatory limit, may be present. Bottled HPLC-grade water, which typically contains 0.5-1 ng NDMA/L, is usually satisfactory. Water obtained from "on-demand" high-purity stills is satisfactory only if the unit is equipped with both reverse-osmosis and UV purification stages.

- NDMA is suitable for neither purge-and-trap analysis or solid-phase extraction with reversed-phase media. This analyte's miscibility with water precludes most extraction procedures with the exception of overnight continuous extraction with dichloromethane and, possibly, extraction with carbonaceous sorbents such as Ambersorb® 572[6].

- High concentrations of neutral species which might interfere with the NDMA determinations were expected in the groundwater samples (normally 1 L volumes employed). These compounds may be removed conveniently with a "pre-extraction" employing a C_{18} Empore® disk conditioned with methanol and water in the usual manner.

- The continuous extraction followed by the usual Kuderna-Danish concentration step can produce an excessive background unless the highest purity solvent, such as Burdick & Jackson "GC²" dichloromethane, is employed.

- Most commercially-available detectors, with the exception of some mass spectrometric detectors, cannot provide adequate sensitivity with a typical 1 or 2 μL sample injection volume. A practical alternative is use a short-path thermal desorber (SPTD) to inject the residues of up to 200 μL sample. Aliquots of the dichloromethane extract, not exceeding 100 μL, are spiked onto a dual-stage carbon sorbent trap; the solvent is removed gently with highest-purity helium. If this procedure is repeated, the residues from up to 200 μL of concentrated extract (one-fifth of the volume available) are concentrated on the trap, and may be injected onto a gas chromatographic column.

- The gas chromatographic column employed must act as both a trap for NDMA and a separation medium to separate the analyte from other components of the extract. In practice, a commercially-available Rtx®-200 column (0.53 mm i.d. x 30 m, 3 μm film thickness) is suitable for both tasks over many (> 1000) injections. Cryotrapping is not necessary if the initial column oven temperature is maintained at 35°C during short-path thermal desorption. Thick-film Stabilwax® columns of similar dimensions and film thickness, while better-known to most chromatographers, exhibit significant column bleed

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during the short-path thermal desorption (performed at 150°C), and are therefore unsuitable for this application.

- Nitrogen phosphorus detectors (NPD) do not possess the selectivity required for determining NDMA at nanogram levels from dichloromethane extracts of aqueous samples. The chemiluminescent nitrogen detector (CLND) provides both the sensitivity and selectivity required. The two-step operating mechanism of the CLND, which explains its selectivity, includes cleavage of the N-N single bond at low furnace temperature (typically 250°C) followed by the chemiluminescent reaction of the NO· free radical with ozone produced in the reaction chamber to form NO_2^*. When NO_2^* degrades to its corresponding ground state, a photon of red light is produced. Under these conditions, this mechanism therefore predicts no expected interferences for the detection of nitrosamines.

- The procedure as described clearly does not lend itself to automated unattended operation, primarily because large sample volumes are needed to achieve the desired sensitivity. For aqueous samples whose NDMA concentrations are known or expected to exceed approximately 100 ng NDMA/L, an automatic sampler can replace the short-path thermal desorber. The two procedures working in tandem permit the determination of NDMA over four orders of magnitude in drinking waters or contaminated groundwaters.

Method Certification and Calculation of the Detection Limit Using the Short-Path Thermal Desorber or Automatic Sampler

The performance of the procedure sketched above was evaluated using protocol developed by the U. S. Army Rocky Mountain Arsenal (RMA) and the U. S. EPA[16,17]. Briefly, the calibration curve was generated using two independently-prepared sets of standards (concentration range 2-160 ng NDMA/mL dichloromethane) analyzed on two separate days. The detector response was plotted against the mass of NDMA expected (in pg). The resulting calibration curve was tested statistically for "lack of fit" compared to linear models with a zero or nonzero intercept. The result was a linear calibration with nonzero intercept, as expected. Two sets of synthetic groundwater samples containing 2-40 ng NDMA/L were generated and analyzed on two separate days. The dichloromethane extract for each sample was concentrated to a final volume of 1 mL, of which 200 μL were ultimately analyzed as described above. Figure 1 shows the respective chromatograms for a synthetic groundwater sample fortified to 10 ng NDMA/L (1A), a synthetic groundwater sample fortified to 2 ng NDMA/L (1B), and a synthetic groundwater blank (1C). A peak was clearly observed for NDMA at the 2 ng/L concentration (Figure 1B) with an area greater than that observed in the synthetic groundwater blank.

The "target" or "expected" mass of NDMA was calculated for each sample, then compared to the "found" mass actually observed, as show in Table 1. A linear regression

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analysis was performed on the data described in Table 1; both upper and lower confidence bands were constructed about the resulting line. The results are shown graphically in Figure 2; the region near the origin is enlarged and depicted in Figure 3.

The "Method Reporting Limit" (MRL), a statistically-based detection limit, was calculated using the data presented in Table 1, and the calculated linear regression line and confidence bands, as depicted in Figures 2 and 3. The MRL value is located by the following four-step procedure: (1) calculate and plot a regression line, representing the "found" vs "target" concentrations, with appropriate two-sided 90% confidence limits for a predicted observation; (2) locate the intercept of the upper 90% predictive confidence limits with the y-axis ("found" concentrations); (3) draw a horizontal line from this intercept until it intersects the lower 90% predictive confidence limits; and (4) draw a vertical line from the intercept described in (3) to the x-axis ("target" concentrations). This intersection with the x-axis is the MRL. Additional details describing the calculation of the MRL are presented elsewhere[18]. The slope of the certification line given in Figure 2, 0.499, may be taken as the overall recovery of NDMA using the procedure (i.e., 50% recovery). In this particular case, the calculated MRL was 348.37 pg NDMA, as shown in Figure 3. This value may be readily converted to approximately 2 ng NDMA/L of synthetic groundwater knowing (a) the NDMA mass, (b) the aqueous sample volume (1 L prepared, 0.9 L analyzed), (c) the dichloromethane concentrate final volume (1 mL), and (d) the volume of (c) used for the determination (200 μL).

$$\frac{348.37 \; pg \; NDMA}{200 \; \mu L \; concentrate} * \frac{1000 \; \mu L \; concentrate}{0.9 \; L \; sample} * \frac{ng \; NDMA}{1000 \; pg \; NDMA} = 1.93 \; ng \; NDMA/L = MRL$$

The "Method Detection Limit" (MDL) was calculated by analyzing eight synthetic groundwater samples (seven required) fortified to 10 ng NDMA/L in the manner described above. The standard deviation, which was calculated for both seven and eight replicates, was then multiplied by the appropriate one-tailed Student's-t statistic for 99% confidence. The resulting value is the MDL, which, in this case, was approximately 2 ng NDMA/L, as shown in Table 2. These calculations also satisfy an additional criterion[16], in that the magnitude of the MRL (1.93 ng NDMA/L, discussed previously) should be equal to or larger than that of the MDL (1.9 ng NDMA/L, given in Table 2).

The MRL, MDL, and overall method recovery were calculated for higher concentrations of NDMA in water in a similar manner, using an automatic sampler to inject 2 μL aliquots of dichloromethane concentrate from 1 L synthetic groundwater samples fortified to 100-2000 ng NDMA/L. The "Target" and "Found" NDMA concentrations from this method certification are presented in Table 3. When the MRL was calculated using all of the data values given in Table 3, a concentration of 272 ng NDMA/mL extract, corresponding to 302 ng NDMA/L groundwater was obtained, considerably greater than the desired 100 ng NDMA/L. The NDMA concentration in the original groundwater sample is calculated knowing the extract concentration (measured), and the volumes of the aqueous sample and dichloromethane concentrate (0.9 L and 1 mL,

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respectively), since

$$\frac{272\ ng\ NDMA}{mL\ concentrate} * \frac{1\ mL\ concentrate}{0.9\ L\ groundwater} = 302\ ng\ NDMA/L = MRL$$

The data set was then truncated by removing the "found" concentrations observed at 2000 ng NDMA/L, as recommended[16]. The MRL calculated using the truncated data set was 103 ng NDMA/mL extract, corresponding to 114 ng NDMA/L groundwater, was obtained. This latter value was close enough to the TRL to be useful; further truncation of the data set was unwarranted. The estimated overall method recovery, based on the slope of the MRL certification graph, was 71%.

The MDL was calculated using eight replicate spiked synthetic groundwater samples (minimum seven required) fortified to 500 ng NDMA/L and the same protocol described previously. The resulting data, presented in Table 4, demonstrate that the calculated MDL, 87 ng NDMA/L, satisfied the criteria for acceptance presented previously.

Application of the "Low-Level" Procedure to the Determination of NDMA in Drinking Water

NDMA was quantitated in three sources of drinking water (four replicates each) and a synthetic groundwater blank using the procedure sketched above. The short-path thermal desorber was used exclusively to inject aliquots of the extract concentrate because the NDMA concentrations expected were below 100 ng NDMA/L. Typical chromatograms are presented in Figure 4, where chromatograms (A) and (B) represent extracts from drinking waters showing 9 and 2 ng NDMA/L, respectively, and chromatogram (C) is the synthetic groundwater blank containing less than 2 ng NDMA/L. The NDMA concentration data, which typically exhibit an RSD <20%, are summarized in Table 5. Values marked with a "J" qualifier exhibit calculated concentrations below the MRL of 2 ng NDMA/L.

Application of the "Low-Level" and "High-Level" Procedures to the Determination of NDMA in Raw and Treated Contaminated Groundwaters

Four sets of raw and treated groundwaters contaminated with NDMA were analyzed using both NDMA procedures described previously. Because the samples were submitted "blind" (i.e., no concentration estimates were provided) and the expected concentrations ranged between 100-5000 ng NDMA/L, all extracts were analyzed initially using the "high-level" procedure featuring the automatic sampler. In this manner, untreated or mildly-treated groundwaters could be identified, quantified, and set aside. Figure 5 shows chromatograms from an untreated groundwater (A), a groundwater which had received some treatment (B), and a synthetic groundwater blank (C). Extracts which exhibited concentrations below 100 ng NDMA/L were

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re-analyzed using the "low-level" procedure, where the short-path thermal desorber was used for sample injection. The chromatograms in Figure 6 show two treated groundwaters (6A and 6B) and a groundwater blank (6C).

The groundwater samples analyzed in this study were "split" and evaluated by an independent collaborating commercial laboratory using a related analytical method. All data is presented in Table 6, and generally shows good to excellent agreement between laboratories over a wide concentration range. The designation "12LT" means that the calculated concentration was less than the commercial laboratory's detection limit, which is 12 ng NDMA/L.

Conclusions

The above discussion demonstrates that the short-path thermal desorber provides a simple and elegant means of injecting the residues from large volumes of organic solvent into a gas chromatograph, thereby providing sensitivity not possible with traditional injectors. Procedures employing the CLND to detect nitrosamines provide additional selectivity compared to the more-common NPD, though less than those using high-resolution mass spectrometry. The method presented permits both a Method Reporting Limit and a Method Detection Limit of 2 ng NDMA/L when the SPTD is in place. A traditional automatic sampler, when substituted for the SPTD, permits unattended analysis of groundwater extracts for NDMA. The MRL and MDL for the latter procedure are approximately 110 and 87 ng NDMA/L, respectively. The procedures have been evaluated using two statistically-based protocols. The two methods taken together were used to analyze NDMA found in various treated groundwaters and drinking water, where the analyte concentrations were expected to range from "trace" (i.e., μg/L) to ultra-trace (i.e., ng/L) levels, or approximately four orders of magnitude. The results from the latter study were compared to, and largely agreed with, those obtained by a commercial analytical laboratory using a different analytical procedure.

Acknowledgements

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Table 1. Comparison of "Target" and "Found" NDMA Masses on the Two Days of Certification Using the Short-Path Thermal Desorber as the Injector

Target NDMA Concentration, ng/L	"Target Mass" NDMA, pg	"Found" Mass of NDMA	
		Day 1	Day 2
2	400	151	288
4	800	402	411
10	2000	1059	993
20	4000	2005	2006
40	8000	4071	3973

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**Table 2. Calculation of the Method Detection Limit Using Replicate Water
Samples Containing 10 ng NDMA/L. Short-Path Thermal Desorber Used as
the Injector.**

Replicate Number	Calculated NDMA, ng/L
1	5.43
2	6.47
3	5.77
4	6.40
5	7.07
6	5.61
7	6.49
8	5.30
Standard deviation, "best" seven samples	0.59
MDL, seven samples[1], ng/L	1.9
Standard deviation, all eight samples	0.63
MDL, eight samples[2]	1.9

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[1]   Student's-t value (one-tailed) at 99% confidence for seven samples (six degrees of
freedom) = 3.143

[2]   Student's-t value (one-tailed) at 99% confidence for eight samples (seven degrees of
freedom) = 2.998

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Table 3. Comparison Between the "Target" and "Found" Concentrations of NDMA When the Automatic Sampler is Used for Sample Injection

"Target" NDMA Concentration, ng/L	"Found" NDMA Concentration, ng/L	
	Day 1	Day 2
100	67	62
200	147	120
500	376	357
1000	745	796
2000	1324	1401

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Table 4. Calculation of the Method Detection Limit Using Replicate Spiked Synthetic Groundwater Samples Containing 500 ng NDMA/L. Automatic Sampler Used as the Injector.

Replicate Number	Calculated Sample Concentration, ng/L
1	369
2	336
3	316
4	348
5	315
6	363
7	389
8	387
Sample standard deviation, "best" seven samples	27
MDL, "best seven samples"[1], ng/L	84
Sample standard deviation, all eight samples	29
MDL, all eight samples[2]	87

[1] Student's-t value (one-tailed) at 99% confidence for seven samples (six degrees of freedom) = 3.143

[2] Student's-t value (one-tailed) at 99% confidence for eight samples (seven degrees of freedom) = 2.998

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Table 5. Determination of NDMA in Drinking Water, Not Corrected for Blank

Source	NDMA, ng/L
A	7.9
	9.3
	9.7
	8.4
Mean, Source A	8.8
Standard deviation, Source A	0.8
B	1.8(J)[1]
	2.6
	2.9
	2.4
Mean, Source B	2.4
Standard deviation, Source B	0.5
C	2.1
	1.8(J)
	1.6(J)
	1.5(J)
Mean, Source C	1.7(J)
Standard deviation, Source C	0.3
Synthetic groundwater blank	1.5(J)

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[1]   Calculated concentration is below the MRL

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Table 6. Comparison of NDMA Determinations Performed by Two Laboratories for Treated and Untreated Groundwater

Sampling Date	Site Designation	NDMA, ng/L		
		"Laboratory A"	ORNL, "High-Level", Autosampler	ORNL, "Low-Level", SPTD
08/06/94	A	280	320	
	B	350	330	
	C	78	41	83
	D	12 (LT)[1]	<110(J)[2]	16
	E	12 (LT)	<110(J)	6
08/06/94	F	260	70(J)[3]	330
	G	12 (LT)	<110(J)	100
	H	12 (LT)	<110(J)	21
	I	12 (LT)	<110(J)	7
08/13/94	J	----[4]	2900	
	K	----	6500	
	L	----	6200	
	M	----	7000	
	N	----	5400	
08/12/94	O	240	270	
	P	12(LT)	<110(J)	27
	Q	300	300	
	R	110	250	

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[1] Concentration is less than (LT) the stated detection limit, 12 ng NDMA/L, of the collaborating laboratory.

[2] No peak detected at all. 110 ng NDMA/L is the MRL; "J" qualifier indicates that the calculated value is below the detection limit.

[3] Improper injection from the automatic sampler led to low calculated value (peak observed, but below the MRL) during the "high-level" procedure. Use data from "low-value" method as final.

[4] Corresponding value from collaborating laboratory not available

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FIGURE CAPTIONS

Figure 1.   Detection of NDMA in (A) synthetic groundwater sample fortified to 10 ng
NDMA/L, (B) synthetic groundwater sample fortified to 2 ng NDMA/L, and (C)
synthetic groundwater blank.

Figure 2.   Graphical Determination of the Method Reporting Limit (MRL) Using All of the
Method Certification Data. (——) = linear regression curve based on the
"found" NDMA masses; (---) = lower confidence limit; (···) = upper confidence
limit; $\bigcirc$ = "found" NDMA mass; $\square$ = MRL.

Figure 3.   Enlargement of the Method Certification Curve Showing the Calculation of the
MRL. (——) = linear regression curve based on the "found" NDMA masses;
(---) = lower confidence limit; (···) = upper confidence limit; $\bigcirc$ = "found"
NDMA mass; (— – —) = steps used to calculate the MRL.

Figure 4.   Detection of NDMA in two sources of drinking water, (A) and (B). The
corresponding synthetic groundwater blank (C) exhibits a smaller concentration
of NDMA than in either source.

Figure 5.   Detection of NDMA in groundwaters using the "high-level" procedure employing
the automatic sampler. (A) and (B) are groundwater extracts; (C) is a synthetic
groundwater blank.

Figure 6.   Detection of NDMA in groundwaters using the "low-level" procedure employing
the short-path thermal desorber. (A) and (B) are groundwater extracts; (C) is a
synthetic groundwater blank.

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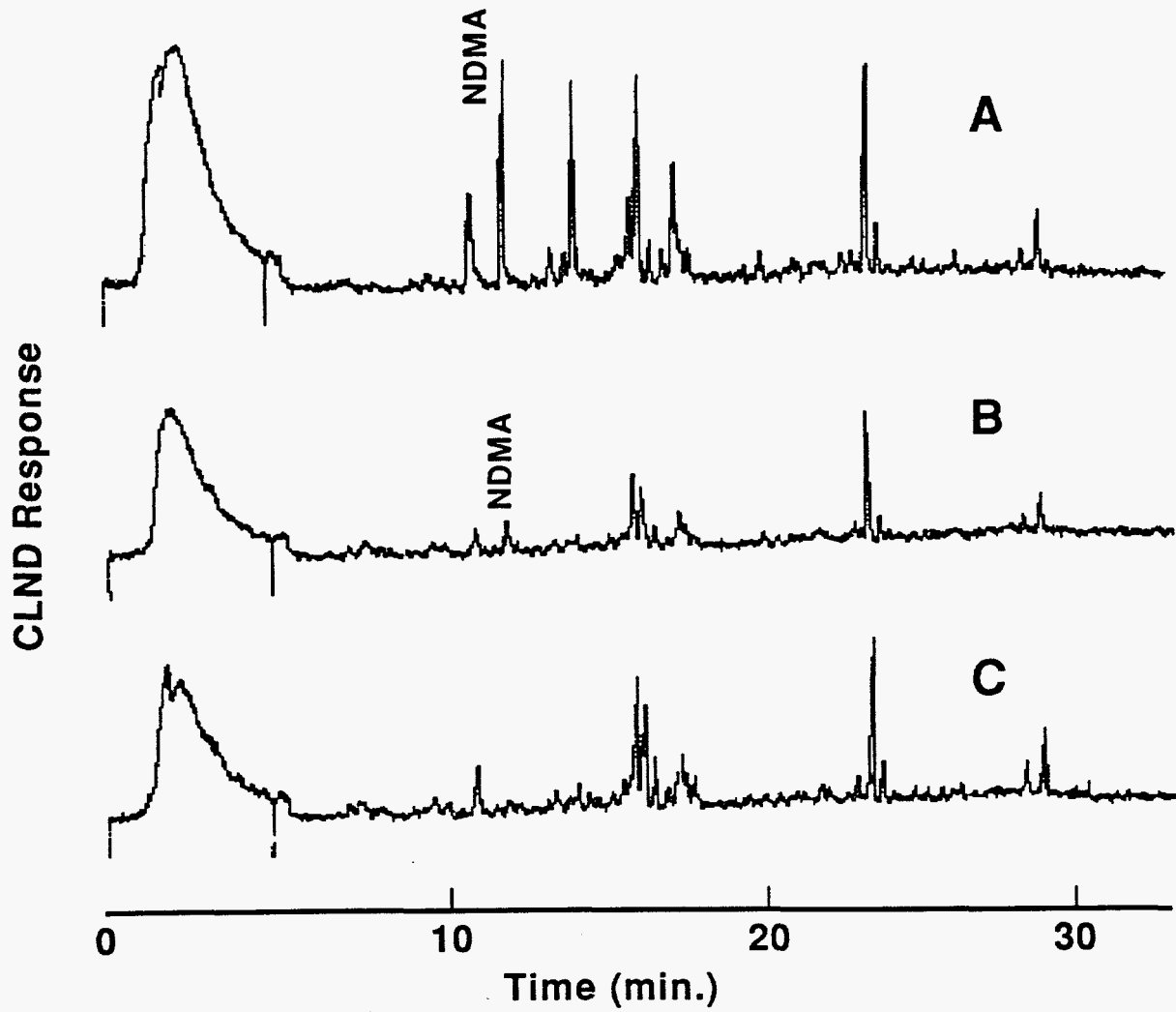Figure 1. Tomkins et al
Top ↑

ORNL-DWG 95Z-4717

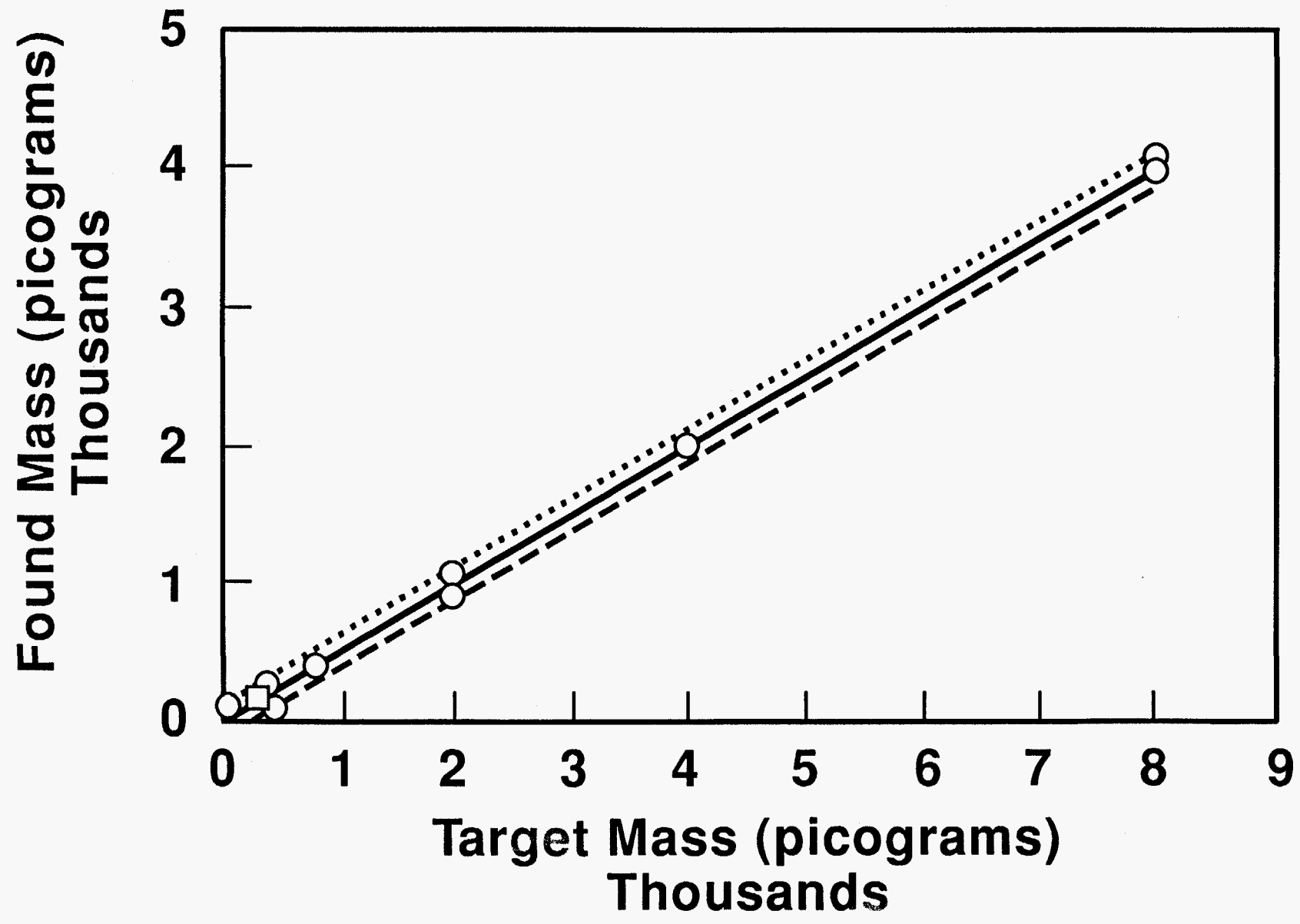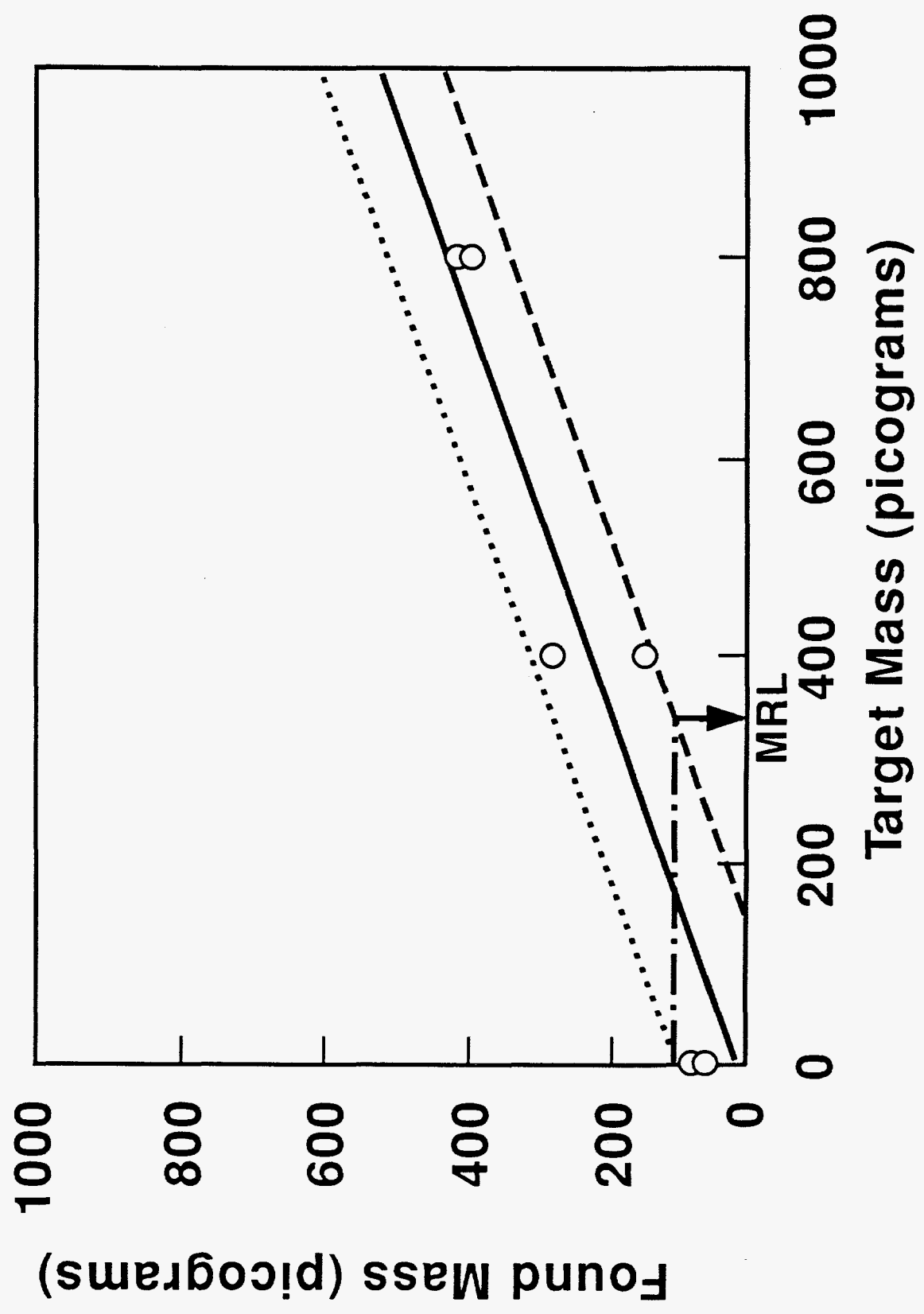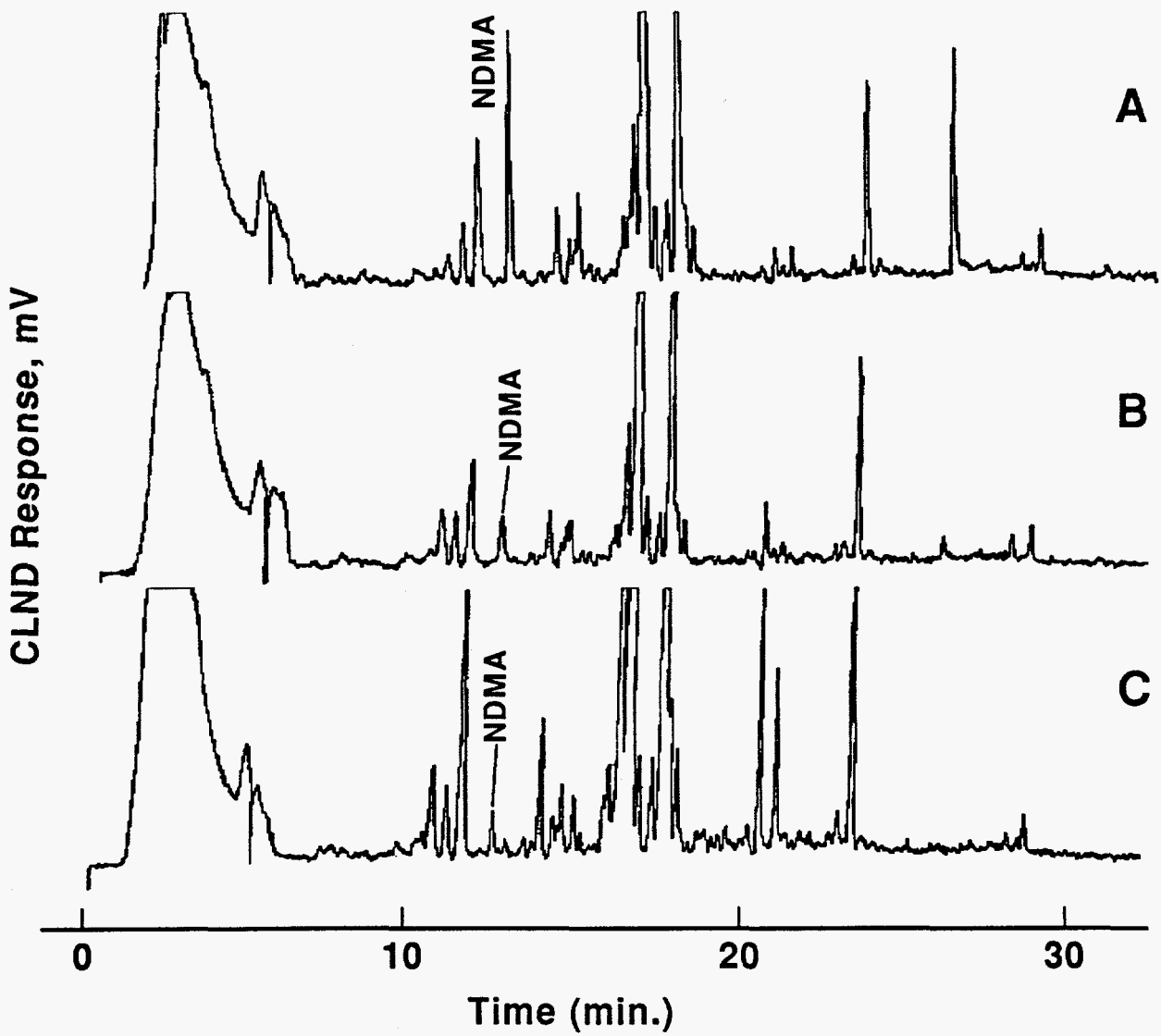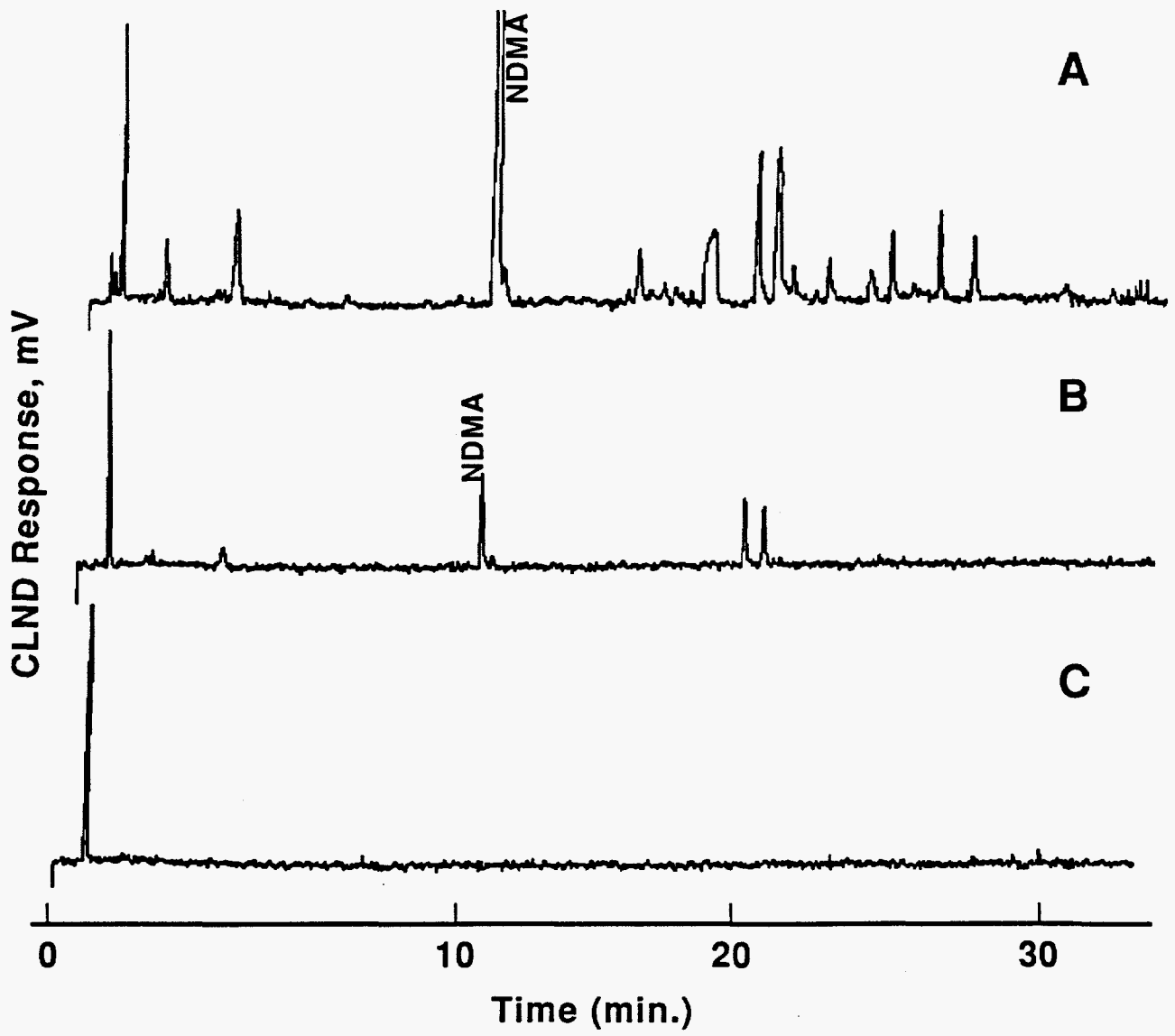Figure 2. Tomkins et al
log ↑

ORNL-DWG 95Z-4716

Figure 3. Tombras et al
log f

ORNL-DWG 95Z-4814

Figure 4. Tonkins et al

Top ↑

Figure 6. Tomkins et al

Top ↑

A

NDMA

B

NDMA

C

NDMA

CLND Response, mV

Time (min.)

0   10   20   30