



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 1582

Petroleum Crude Oil

This Standard Reference Material (SRM) is intended for use in evaluating analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs), hopanes, and steranes in a crude oil matrix. All of the constituents for which certified and reference values are provided are naturally present in the oil. A unit of SRM 1582 consists of five ampoules, each containing approximately 1.2 mL of crude oil.

Certified Mass Fraction Values: Certified values for 20 PAHs are provided in Table 1. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [1]. The certified values are based on the agreement of results obtained at NIST using multiple analytical techniques.

Reference Mass Fraction Values: Reference values are provided in Table 2 for 18 additional PAHs, in Table 3 for 35 groups of alkylated PAHs, and in Table 4 for 15 hopanes and steranes. Reference values are noncertified values that are the best estimate of the true value; however, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [1].

Expiration of Certification: The certification of **SRM 1582** is valid, within the measurement uncertainty specified, until **30 September 2020**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see “Instructions for Handling, Storage, and Use”). This certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The overall direction and coordination of technical measurements leading to the update of the certification of SRM 1582 were performed by M.M. Schantz and L.C. Sander of the NIST Analytical Chemistry Division.

Analytical measurements at NIST to update SRM 1582 were performed by B.A. Benner, Jr., J.R. Kucklick, and M.M. Schantz of the NIST Analytical Chemistry Division. Additional results for PAHs, hopanes, and steranes were used from 24 laboratories (see Appendix A) that participated in an interlaboratory study coordinated by M.M. Schantz of the NIST Analytical Chemistry Division.

Evaluation of the data was provided by N.A. Heckert, S.D. Leigh, and A.L. Pintar of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Robert L. Watters, Jr., Chief
Measurement Services Division

Gaithersburg, MD 20899
Certificate Issue Date: 26 June 2012
Certificate Revision History on Page 7

INSTRUCATIONS FOR HANDLING, STORAGE, AND USE

Handling: This material is naturally occurring crude oil and may contain constituents of unknown toxicities; therefore, caution and care should be exercised during its handling and use. Consult the Material Safety Data Sheet (MSDS), enclosed with the SRM shipment, for details.

Storage: Sealed ampoules, as received, should be stored in the dark at temperatures between 10 °C and 30 °C.

Use: Samples for analysis should be withdrawn immediately after opening ampoules and should be processed without delay for the certified values in Table 1 to be valid within the stated uncertainties. Certified values are not applicable to material stored in ampoules that have been opened, even if they are resealed.

PREPARATION AND ANALYSIS⁽¹⁾

Sample Collection and Preparation: The petroleum crude oil for this SRM came from the U.S. Environmental Protection Agency's repository at the Oak Ridge National Laboratory, Oak Ridge, TN. The oil was homogenized by stirring for 18 h in a 6 L glass flask before transferring into 5 mL amber glass ampoules which had been flushed with argon.

PAHs, Hopanes, and Steranes: The general approach used for the value assignment of the PAHs, hopanes, and steranes in SRM 1582 consisted of combining results from analyses using various combinations of different cleanup/isolation procedures and chromatographic separation and detection techniques [2].

Three sets of gas chromatography/mass spectrometry (GC/MS) results, designated as GC/MS (I) through GC/MS (III), were obtained at NIST. For GC/MS (I) analyses, duplicate test portions of 400 mg from three ampoules of SRM 1582 were transferred to individual vials, spiked with a known amount of an internal standard solution (see below), and diluted with hexane. A portion of the diluted oil (0.5 mL) was fractionated using an aminopropyl solid-phase extraction (SPE) column to isolate the fraction of interest. Following a concentration step, the processed extract was then fractionated using liquid chromatography on a semi-preparative scale aminopropyl silane column. Three fractions were collected: (1) aliphatics, hopanes, and steranes; (2) naphthalene through the dimethylphenanthrenes and anthracenes; and (3) the remainder of the PAHs through molecular mass 302 Da. Each fraction was then analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with a 50 % (mole fraction) phenyl methylpolysiloxane phase (0.25 µm film thickness; DB-17MS, Agilent Technologies, Wilmington, DE). Fractions 2 and 3 were also analyzed using a 0.25 mm i.d. × 15 m fused silica capillary column with a 50 % (mole fraction) liquid crystal polysiloxane phase (0.15 µm film thickness; LC-50, J&K Scientific, Milton, Ontario, Canada). The results from the DB-17MS column are denoted as GC/MS Ia and those from the LC-50 column as GC/MS Ib.

For the GC/MS (II) determination of the PAHs, one test portion (90 mg to 100 mg) from each of six ampoules was transferred to a vial, spiked with a known amount of internal standard solution (see below), and diluted with 2 % dichloromethane in hexane (volume fractions). A portion of the diluted oil (0.1 mL) was fractionated using an aminopropyl solid-phase extraction (SPE) column to isolate the fraction of interest. Following a concentration step, the isolated fraction was analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with a 50 % phenyl methylpolysiloxane phase (0.25 µm film thickness; ZB-50 column, Phenomenex, Torrance, CA).

For the GC/MS (III) determination of the PAHs, hopanes, and steranes, one test portion (1 mL, exact mass known) from each of three ampoules was transferred to a bottle and diluted with 25 mL of hexane (exact mass known) prior to adding the internal standards (see below). The extracts were fractionated into two fractions using a silica/alumina column with the majority of the aliphatics, hopanes, and steranes in fraction 1 and the majority of the PAHs in fraction 2. The analytes of interest were quantified using GC/MS on a 0.25 mm i.d. × 60 m fused silica capillary column with a 50 % (mole fraction) phenyl methylpolysiloxane phase (0.25 µm film thickness; Rxi-17sil MS, Restek, Bellefonte, PA).

For the methods described above, selected perdeuterated PAHs and perdeuterated aliphatics were added to the crude oil as described above for use as internal standards for quantification purposes.

In addition to the analyses performed at NIST, SRM 1582 was used in an interlaboratory comparison exercise in 2011 [3]. Results from 24 laboratories that participated in this exercise were used as the fourth data set in the

⁽¹⁾ Certain commercial equipment, instruments or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

determination of the values for PAHs, hopanes, and steranes in SRM 1582. Note that not all laboratories returned data for each analyte. The laboratories participating in this exercise used the analytical procedures routinely used in their laboratories to measure the analytes of interest. For the alkylated PAHs, the majority of the laboratories (>90 %) used the parent PAH for determination of the response factor for the corresponding alkylated group.

Homogeneity Assessment for PAHs: The homogeneity of SRM 1582 was assessed during the original certification study. No differences among ampoules were observed for the PAHs at the 100 mg sample size.

Table 1. Certified Mass Fraction Values for Selected PAHs in SRM 1582

	Mass Fraction mg/kg	<i>k</i>
Naphthalene ^(a,b,c,d)	153 ± 13 ^(e)	
1-Methylnaphthalene ^(a,b,d)	348 ± 15 ^(f)	1.97
2-Methylnaphthalene ^(a,b,d)	547 ± 56 ^(e)	
Phenanthrene ^(a,b,c,d,g)	99 ± 15 ^(f)	1.97
1-Methylphenanthrene ^(a,b,c,g)	80.1 ± 8.3 ^(e)	
2-Methylphenanthrene ^(a,b,c,g)	125.0 ± 5.2 ^(e)	
3-Methylphenanthrene ^(a,b,c,g)	104 ± 11 ^(e)	
9-Methylphenanthrene ^(a,b,c,g)	110.1 ± 5.0 ^(f)	1.96
Fluoranthene ^(a,b,c,d,g)	3.62 ± 0.78 ^(f)	1.97
Pyrene ^(a,b,c,d,g)	11.9 ± 1.4 ^(e)	
Benz[<i>a</i>]anthracene ^(a,b,c,g)	3.63 ± 0.45 ^(e)	
Chrysene/Triphenylene ^(a,b,d,h)	18.2 ± 1.4 ^(e)	
Benzo[<i>b</i>]fluoranthene ^(a,b,c,g)	2.66 ± 0.30 ^(e)	
Benzo[<i>e</i>]pyrene ^(a,b,c,d,g)	3.98 ± 0.57 ^(f)	1.98
Benzo[<i>a</i>]pyrene ^(a,b,c,d,g)	1.07 ± 0.15 ^(e)	
Perylene ^(a,b,c,d,g)	30.0 ± 1.7 ^(e)	
Benzo[<i>ghi</i>]perylene ^(a,b,c,g)	1.75 ± 0.20 ^(e)	
Dibenz[<i>a,h</i>]anthracene ^(b,c,g)	0.594 ± 0.021 ^(e)	
Picene ^(b,c)	0.842 ± 0.038 ^(e)	

^(a) GC/MS Ia using LC fractionation followed by analysis on a DB-17MS column.

^(b) GC/MS II using SPE clean-up followed by analysis on a ZB-50 column.

^(c) GC/MS III using silica/alumina fractionation followed by analysis on an Rxi-17sil MS column.

^(d) Data from the interlaboratory study [3].

^(e) The certified value is a weighted mean of average mass fractions, with one average each from two to five analytical methods [4,5]. The standard uncertainty is the estimated standard deviation of the sampling distribution of the weighted mean [5,6]. The expanded uncertainty is twice the standard uncertainty, which is consistent with the ISO Guide [7,8].

^(f) The certified value is a weighted mean of average mass fractions, with one average each from two to five analytical methods [4,5]. The expanded uncertainty is the half width of a symmetric 95 % parametric bootstrap confidence interval [9], and is consistent with the ISO Guide [7,8]. The effective coverage factor *k* is given above.

^(g) GC/MS Ib using LC fractionation followed by analysis on an LC-50 column.

^(h) Chrysene and triphenylene co-elute under the GC conditions used for these measurements.

Table 2. Reference Mass Fraction Values for Selected PAHs in SRM 1582

	Mass Fraction mg/kg
Biphenyl ^(a,b,c,d)	27.9 ± 1.5 ^(e)
Acenaphthene ^(a,b,c,d)	23.9 ± 7.5 ^(e)
1,6-Dimethylnaphthalene ^(a,b)	477 ± 88 ^(e)
1,6,7-Trimethylnaphthalene ^(f)	250 ± 40 ^(g)
Fluorene ^(a,b,c,d)	37 ± 11 ^(e)
Dibenzothiophene ^(a,b,c,d)	46 ± 15 ^(e)
Anthracene ^(a,g)	2.50 ± 0.16 ^(e)
2-Methylanthracene ^(b,c)	10.2 ± 1.6 ^(e)
1,7-Dimethylphenanthrene ^(a,b,c,f)	115 ± 29 ^(e)
1-Methylfluoranthene ^(f)	4.18 ± 0.22 ^(g)
3-Methylfluoranthene ^(f)	0.59 ± 0.12 ^(g)
1-Methylpyrene ^(a,b,c,f)	10.4 ± 3.2 ^(e)
4-Methylpyrene ^(a,b,c,f)	15.6 ± 1.6 ^(e)
Triphenylene ^(c,f)	6.82 ± 0.17 ^(e)
6-Methylchrysene ^(a,b,c,f)	8.24 ± 0.75 ^(e)
Benzo[<i>j</i>]fluoranthene ^(a,f)	0.610 ± 0.042 ^(e)
Dibenz[<i>a,c</i>]anthracene ^(b)	0.85 ± 0.20 ^(g)
Benzo[<i>b</i>]chrysene ^(c)	0.288 ± 0.037 ^(g)

^(a) GC/MS Ia using LC fractionation followed by analysis on a DB-17MS column.

^(b) GC/MS II using SPE clean-up followed by analysis on a ZB-50 column.

^(c) GC/MS III using silica/alumina fractionation followed by analysis on an Rxi-17sil MS column.

^(d) Data from the interlaboratory study [3].

^(e) The reference value is a weighted mean of the average mass fractions, with one average each from two to four analytical methods [4,5]. The standard uncertainty is the estimated standard deviation of the sampling distribution of the weighted means [5,6]. The expanded uncertainty is twice the standard uncertainty, which is consistent with the ISO Guide [7,8].

^(f) GC/MS Ib using LC fractionation followed by analysis on a LC-50 column.

^(g) The reference mass fraction value is the mean of results using one analytical technique. The expanded uncertainty, U , is calculated as $U = ku_c$, where u_c is one standard deviation of the analyte mean, and the coverage factor, k , is determined from the Student's t -distribution corresponding to the associated degrees of freedom and a 95 % confidence level for each analyte. Degrees of freedom: 15 for 2,6,7-trimethylnaphthalene and 2 for 1-methylfluoranthene, 3-methylfluoranthene, dibenz[*a,c*]anthracene, and benzo[*b*]chrysene.

Table 3. Reference Values for Selected Alkylated PAH Groups in SRM 1582

	Mass Fraction ^(a) mg/kg	Degrees of Freedom
C1-decalins	860 ± 300	6
C2-decalins	1530 ± 610	5
C3-decalins	1460 ± 600	5
C4-decalins	860 ± 330	5
C1-naphthalenes	620 ± 90	20
C2-naphthalenes	1100 ± 170	21
C3-naphthalenes	1100 ± 200	20
C4-naphthalenes	770 ± 150	20
C1-benzothiophenes	48 ± 6	6
C2-benzothiophenes	91 ± 30	6
C3 benzothiophenes	160 ± 30	5
C4-benzothiophenes	140 ± 20	5
C1-fluorenes	120 ± 20	19
C2-fluorenes	230 ± 40	19
C3-fluorenes	230 ± 20	20
C1-phenanthrenes/anthracenes	350 ± 50	22
C2-phenanthrenes/anthracenes	470 ± 50	21
C3-phenanthrenes/anthracenes	430 ± 50	20
C4-phenanthrenes/anthracenes	230 ± 40	17
C1-dibenzothiophenes	120 ± 16	21
C2-dibenzothiophenes	190 ± 30	21
C3-dibenzothiophenes	170 ± 20	19
C4-dibenzothiophenes	100 ± 20	16
C1-fluoranthenes/pyrenes	52 ± 7	19
C2-fluoranthenes/pyrenes	96 ± 10	16
C3-fluoranthenes/pyrenes	120 ± 20	18
C4-fluoranthenes/pyrenes	110 ± 30	10
C1-naphthobenzothiophenes	62 ± 17	7
C2-naphthobenzothiophenes	84 ± 18	7
C3-naphthobenzothiophenes	79 ± 18	6
C4-naphthobenzothiophenes	52 ± 26	6
C1-benzanthracenes/chrysenes/triphenylenes	54 ± 5	17
C2-benzanthracenes/chrysenes/triphenylenes	100 ± 15	18
C3-benzanthracenes/chrysenes/triphenylenes	92 ± 16	17
C4-benzanthracenes/chrysenes/triphenylenes	78 ± 18	14

^(a) The reference mass fraction value is the mean of results from the interlaboratory study [3]. The expanded uncertainty, U , is calculated as $U = ku_c$, where u_c is one standard deviation of the analyte mean, and the coverage factor, k , is determined from the Student's t -distribution corresponding to the associated degrees of freedom and a 95 % confidence level for each analyte.

Table 4. Reference Values for Selected Hopanes and Steranes in SRM 1582

	Mass Fraction mg/kg
17 α (H)-22,29,30-Trisnorhopane ^(a,b,c)	48.0 \pm 4.9 ^(d)
17 α (H), 21 β (H)-30-Norhopane ^(a,b,c)	142 \pm 15 ^(d)
18 α (H)-22,29,30-Trisnorhopane ^(c)	20.1 \pm 3.4 ^(e)
17 α (H), 21 β (H)-30-Hopane ^(a,b,c)	283 \pm 47 ^(d)
17 α (H), 21 β (H)-22R-Homohopane ^(a,b,c)	85 \pm 18 ^(d)
17 α (H), 21 β (H)-22S-Homohopane ^(a,b,c)	100 \pm 34 ^(d)
13 β (H),17 α (H)-Diacholestane 20S ^(c)	96 \pm 23 ^(e)
5 α (H), 14 α (H),17 α (H)-Cholestane 20S ^(c)	233 \pm 50 ^(e)
5 α (H), 14 α (H),17 α (H)-Cholestane 20R ^(a,b,c)	270 \pm 150 ^(d)
5 α (H), 14 α (H),17 α (H)-24-Ethylcholestane 20S ^(c)	223 \pm 63 ^(e)
5 α (H), 14 α (H),17 α (H)-24-Ethylcholestane 20R ^(a,b,c)	116 \pm 47 ^(d)
5 α (H), 14 β (H),17 β (H)-Cholestane 20S ^(c)	174 \pm 38 ^(e)
5 α (H), 14 β (H),17 β (H)-Cholestane 20R ^(a,b,c)	173 \pm 20 ^(d)
5 α (H), 14 β (H),17 β (H)-24-Ethylcholestane 20S ^(c)	115 \pm 28 ^(e)
5 α (H), 14 β (H),17 β (H)-24-Ethylcholestane 20R ^(c)	116 \pm 47 ^(e)

^(a) GC/MS Ia using LC fractionation followed by analysis on a DB-17MS column.

^(b) GC/MS III using silica/alumina fractionation followed by analysis on an Rxi-17sil MS column.

^(c) Data from the interlaboratory study [3].

^(d) The reference mass fraction value is a weighted mean of the mass fractions from three analytical methods [4]. The uncertainty listed with each value is an expanded uncertainty about the mean [4,5], with coverage factor, $k = 2$, calculated by combining within-method variances with a between-method variance [6] following the ISO Guide [7,8].

^(e) The reference mass fraction value is the mean of results using one analytical technique. The expanded uncertainty, U , is calculated as $U = ku_c$, where u_c is one standard deviation of the analyte mean, and the coverage factor, k , is determined from the Student's t -distribution corresponding to eight degrees of freedom and a 95 % confidence level for each analyte.

REFERENCES

- [1] May, W.; Parris, R.; Beck, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136; U.S. Government Printing Office: Washington, DC (2000); available at <http://www.nist.gov/srm/publications.cfm> (accessed June 2012).
- [2] Wise, S.A.; Poster, D.L.; Kucklick, J.R.; Keller, J.M.; VanderPol, S.S.; Sander, L.C.; Schantz, M.M.; *Standard Reference Materials (SRMs) for Determination of Organic Contaminants in Environmental Samples*; Anal. Bioanal. Chem., Vol. 386, pp. 1153-1190 (2006).
- [3] Schantz, M.M.; Kucklick, J.R.; *NIST Interlaboratory Analytical Comparison Study to Support Deepwater Horizon Natural Resource Damage Assessment: Description and Results for Crude Oil QA10OIL01*; NISTIR 7793 National Institute of Standards and Technology, U.S. Department of Commerce: Gaithersburg, MD (2011).
- [4] Dersimonian, R.; Laird, N.; *Meta-Analysis in Clinical Trials*; Control Clin. Trials, Vol. 7, pp. 177-188 (1986).
- [5] Rukhin, A.L.; *Weighted Means Statistics in Interlaboratory Studies*; Metrologia, Vol. 46, pp. 323-331 (2009).
- [6] Horn, R.A.; Horn, S.A.; Duncan, D.B.; *Estimating Heteroscedastic Variance in Linear Models*; J. Am. Stat. Assoc., Vol. 70, pp. 380-385 (1975).
- [7] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement (ISO GUM 1995 with Minor Corrections)*; Joint Committee for Guides in Metrology (2008); available at http://www.bipm.org/utis/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed June 2012); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at <http://www.nist.gov/pml/pubs/tn1297/index.cfm> (accessed June 2012).
- [8] JCGM 101:2008; *Evaluation of measurement data – Supplement 1 to the Guide to Expression of Uncertainty in Measurement*; Propagation of Distributions Using a Monte Carlo Method; Joint Committee for Guides in Metrology (BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML), International Bureau of Weights and Measures (BIPM), Sèvres, France (2008); available at http://www.bipm.org/utis/common/documents/jcgm/JCGM_101_2008_E.pdf (accessed June 2012).
- [9] Efron, B.; Tibshirani, R.J.; *An Introduction to the Bootstrap*; Chapman & Hall (1993).

Certificate Revision History: 26 June 2012 (Updated certified mass fraction values for six PAHs, and added new certified and reference values for additional PAHs, alkylated PAHs, hopanes, and steranes; added expiration date; editorial changes); 23 January 1984 (Original certificate date).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at <http://www.nist.gov/srm>.

APPENDIX A

The analysts and laboratories listed below participated in the interlaboratory comparison exercise for the determination of PAHs, hopanes, and steranes in SRM 1582 [3].

E. Porta, Alpha Analytical, Inc., Mansfield, MA, USA
D. Birkholz and S. Stilson, ALS Environmental Division, Edmonton, AB, Canada
K. Krahforst, Battelle Analytical & Environmental Chemistry Laboratory, Duxbury, MA, USA
J. Wiegel and K. Fedele, Columbia Analytical Services, Jacksonville, FL, USA
M. Perry, Columbia Analytical Services, Rochester, NY, USA
G. Salata and J. Gish, Columbia Analytical Services, Kelso, WA, USA
P. Gardinali, Florida International University, North Miami, FL, USA
K. Aldous and S. Shaver, New York State Department of Health, Albany, NY, USA
E. Wirth, NOAA/NCCOS/NOS, Charleston, SC, USA
M. Carls and M. Larsen, NOAA/NMFS/Alaska Fisheries Science Center, Juneau, AK, USA
J. Bolton, C. Sloan, G. Yitalo, NOAA/NMFS/NW Fisheries Science Center, Seattle, WA, USA
C. Nowlan, Pace Analytical Services, Inc., Minneapolis, MN, USA
K. Rickabaugh, A. Levine, S. Schlager, RJ Lee Group, Inc., Monroeville, PA, USA
Y. Yohannes, RJ Lee Group, Inc., Pasco, WA, USA
J. Ramirez, TDI/B&B Laboratories, Inc., College Station, TX, USA
C. Newton and E. Schellinger, TestAmerica Laboratories, Mobile, AL, USA
K. Buechler and S. Rogers, TestAmerica Laboratories, West Sacramento, CA, USA
M. Healy, T. Preston, G. Rynker, G. Swaney, TestAmerica Laboratories, University Park, IL, USA
L. Matko and S. Bacha, TestAmerica Laboratories, Pittsburgh, PA, USA
T. Yoder and B. Wagner, TestAmerica Laboratories, Knoxville, TN, USA
B. Stearns, TestAmerica Laboratories, South Burlington, VT, USA
K. Kreps and C. McKean, TestAmerica Laboratories, Tacoma, WA, USA
J. Sericano and T. Wade, Texas A&M University, College Station, TX, USA
T. Cain and M. Wichman, University of Iowa, Iowa City, IO, USA