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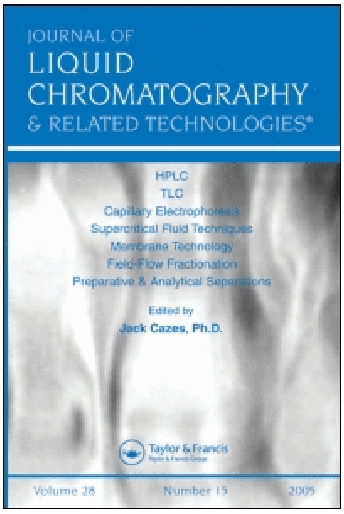

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
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To cite this Article Nesterenko, P. and Jones, P.(1996) 'The Comparative Investigation of Several Stationary Phases Containing Iminodiacetic Functional Groups for the High Performance Chelating Exchange Chromatography', Journal of Liquid Chromatography & Related Technologies, 19: 7, 1033 — 1045

To link to this Article: DOI: 10.1080/10826079608006300

URL: http://dx.doi.org/10.1080/10826079608006300

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J. LIQ. CHROM. & REL. TECHNOL., 19(7), 1033–1045 (1996)

THE COMPARATIVE INVESTIGATION OF SEVERAL STATIONARY PHASES CONTAINING IMINODIACETIC FUNCTIONAL GROUPS FOR THE HIGH PERFORMANCE CHELATING EXCHANGE CHROMATOGRAPHY

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ABSTRACT

Three chelating ion-exchangers having iminodiacetic acid functional groups immobilised at the surface of different substrates (silica gel, hydrophilic and hydrophobic polymer matrices) were compared for the separation of various alkaline-earth and transition metal ions. The retention of metal ions on two commercially available Diasorb IDA silica (250 mm x 4 mm id.) and Tosoh TSK Gel Chelate 5 PW (75 x 7 mm id.) columns and column packed with poly(styrene-divinylbenzene) substrate coated with Phthalein Purple dye was investigated in maleate, tartrate and oxalate mobile phases. Metal-ion retention increased

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with pH and with a decrease in eluent concentration. The complexing ability of ion-exchangers decreased in the order IDA-silica > TSK Gel Chelate 5 PW > polystyrene-divinylbenzene coated with Phthalein Purple dye. The selectivity of separation was similar for IDA-silica and TSK Gel Chelate 5 PW and was slightly different for the dye coated column. The chromatographic separation of metal ions is demonstrated in oxalate and tartrate mobile phases.

INTRODUCTION

Chelating ion exchangers containing iminodiacetic acid (IDA) functional groups have been widely used for the preconcentration of traces of transition metal ions from waters with complex matrices. Their main advantages are good selectivity and good kinetics of complexation. The latter property allows the application of iminodiacetic acid containing sorbents for the on-line preconcentration and also for the direct chromatographic separation of metal ions.

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In the last decade a great interest in the application of different iminodiacetic acid containing ion-exchangers for the ion-chromatographic separation of metals has appeared.[1-10] The application of octadecylsilica dynamically modified with dodecyliminodiacetic acid for the isocratic separation of alkaline-earth metal ions was described.[1] The tartrate eluent was used for the separation of four metals. The covalent attachment of iminodiacetic acid to the polymer or silica surface produced chelating phases of increased working stability. Thus, Toei[2] used the commercially available polymer based column TSK-Gel Chelate 5-PW bearing IDA groups. The separation of magnesium, calcium and strontium was achieved with o-cresol-phtalein complexone as a component of the mobile phase and magnesium and calcium were determined in sea water. It should be noted this column packing was originally designed for the metal-chelate affinity chromatography of proteins and peptides in neutral media so its stability in acid eluent was suspect.

This problem can be overcome by using silica based sorbents. The higher stability with good separation efficiency and selectivity for alkaline, alkaline-earth and transition metals has been demonstrated for iminodiacetic acid bonded silica.[3-5] It was found that both complexation reactions and ion-exchange interactions occurred on the stationary phase. As a result, the ion-chromatographic separation of alkaline, alkaline earth and transition metal ions was possible with different mineral and organic acids used as the eluent.

chromatographic separation of alkaline, alkaline earth and transition metal ions was possible with different mineral and organic acids used as the eluent.

Another type of chelating ion-exchanger with IDA groups was investigated by Jones and co-workers.[6-10] He studied a number of HPLC resins impregnated with dyes containing iminodiacetic acid functional groups such as Xylenol Orange,[6-9] Methyl thymol Blue[6-10] and Phthalein Purple.[10] These Methylthymol chelating ion-exchangers proved to be extremely successful for the separation of a number of alkaline earth and transition metal ions using step gradient elution. The application of impregnated resins to the chromatographic determination of different metal ions in concentrated brines, sea water was described. To decrease the influence of complex matrices on the concentration and the separation of metal ions the eluents of increased ionic strength (0.5 - 1.0 M solutions of KNO_3 or KCl) were used. It allowed the supression of the ion-exchange equilibria in chromatographic systems and therefore to use mainly the chelating ability of resins coated with dyes for the separation.

So, it can be seen that the several chromatographic approaches including chelating ion-exchangers with IDA groups have been studied. However, in order to establish the general properties and the optimal substrates for the high-performance separation of transition metal ions, more detailed investigations are required. In this study three different types of iminodiacetic acid containing ion-exchangers and their metal-ion chromatographic behaviour were evaluated.

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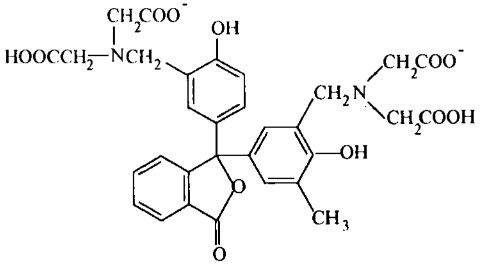
MATERIALS

Apparatus

An isocratic ion-chromatographic system consisted of LKB 2150 HPLC titanium pump (Bromma, Sweden), a Rheodyne 7010 polyether-ether-ketone (PEEK) liquid six port injection valve (Rheodyne, Cotati, CA, USA) fitted with 100 µL PEEK sample loop and post-column detection system. The latter included a Constametric III HPLC pump (LDC, Riviera Beach, Fl, USA) used for delivery of 4-(2-pyridylazo)-resorcinol (PAR) reagent, a zero dead volume PTFE tee followed by a 1.4 m, 0.3 mm ID PTFE reaction coil and Dionex Spectral Array detector (Dionex, Sunnyvale, CA, USA) set at 490 nm.

Columns

Tosoh (Tokyo, Japan) and JV BioChemmack (Moscow, Russian Federation),



$pK_1 = 2.2$
$pK_2 = 2.9$
$pK_3 = 7.0$
$pK_4 = 7.8$
$pK_5 = 11.4$
$pK_6 = 12.0$

Figure 1. The structure and pK values of Phthalein Purple.

correspondingly.

Phthalein Purple (Sigma Chemicals, Poole, UK) was used to impregnate 8.8 μm particle size polystyrene divinylbenzene neutral hydrophobic resin (Dionex, Sunnyvale, CA, USA). The modified resin was packed in a 100 x 4.6mm ID PEEK column.

Reagents

Phthalein Purple (Sigma Chemicals, Poole, UK) or *o*-Cresolphthalein-3',3"-bis-methyleniminodiacetic acid (Fig. 1) was used for impregnation of polystyrene divinylbenzene neutral hydrophobic resin. Common reagents were supplied by BDH (Poole, UK) except PAR and Zn-EDTA which were obtained from Fluka (Glossop, UK). Metal stock solutions were Spectrosol standard solutions obtained from BDH. Other reagents were of analytical grade. All solutions were prepared using deionised water from Milli-Q system (Millipore, Bedford, MA, USA).

RESULTS AND DISCUSSION

Comparative Characteristics of Chelating Ion-exchangers

As described earlier the nature of bonded chelating agent is a key factor responsible for the selectivity of the stationary phase. IDA exhibits both ion-exchange properties for metal ions attributed to free carboxylate groups and a

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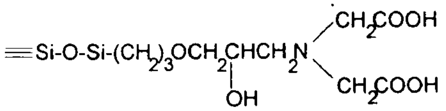
Table 1

Characteristics of Chelating Sorbents Containing Iminodiacetic Acid Functionality

N	Name	Particle Size, μm	Diameter Pore, nm	Matrice	pH Range Stability	Concentration of Ligand μMole/g	Capacity for Transition Metals
1	Tosoh TSK Gel Chelate 5-PW	10	100	hydrophilc polymer*	2-12		24 μmole/ml Cu(II)[12]
2	IDA-silica	6	15	silica	1-7	130	
3	Phtalein Purple	8.8	12	neutral PST-DVB	0.5-11	157	22.1 μmole/g Zn(II)

strong complexing property especially for transition metal ions due to the formation of a stable 6-member ring complex including nitrogen and carboxylic groups. According to literature data the complexing ability of Phthalein Purple molecules is lower than N-alkylsubstituted iminodiacetic acid.[11] The type of immobilisation of molecules at the surface of substrates determines the availability of IDA groups for binding of metal ions. So, one can conclude from Table 1, only 14 mole% of the dye was "active" assuming 1:1 ratio of metal to ligand binding.

Besides the type of immobilisation of IDA groups at the surface of the matrix, the concentration of immobilised ligands, their distribution at the surface and the nature of matrix can also impact on the selectivity of separation. Some of above properties of studied IDA chelating ion-exchangers are presented in Table 1. As can be seen from Table 1 the studied sorbents have hydrophilic and hydrophobic polymers and silica as a backbone. Nevertheless, both the concentration of immobilised ligand and the capacity of studied chelating exchangers have similar magnitudes. It should mean equal retention for columns of equal volume assuming similar complexing ability. Practically equal values of column volume were calculated for TSK-Gel Chelate 5 PW column and IDA-silica column namely 3.3 mL and 3.14 mL, respectively. The volume of the Phthalein Purple column was about 2.5 times smaller.



$$\equiv Si\text{-}O\text{-}Si\text{-}(CH_2)_3OCH_2CH(OH)CH_2N(CH_2COOH)_2$$

$pK_1 = 2.12$

Figure 2. The structure of silica based chelating ion-exchanger

The main drawbacks of polymeric substrates are swelling and shrinking with change in pH and ionic strength of eluent. However, both the hydrophilic polymer in the case of TSK Gel Chelate 5PW and polystyrene- divinylbenzene neutral hydrophobic resin coated with Phthalein Purple had no tendency for volume change in various eluents.

It would be expected a litttle difference in acid-base properties for Phthalein Purple (Fig. 1) in solution and in immobilised state at the polymer surface. In case of iminodiacetic acid covalently bonded to silica (Fig. 2) the change in acid-base properties of chelating ion-exchangers is possible due to secondary interactions with residual silanol groups.

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Dependence of Retention of Transition Metal Ions on Concentration of Eluent

The selectivity of chelating exchangers and the retention of transition metal ions can be controlled by altering the conventional stability constants of the chelates, through the pH of the eluent or through the concentration of complexing acid in the eluent. The solutions of dicarboxylic acids of different complexing and acidic ability (maleic, tartaric and oxalic) were used as eluents for some transition metal ions. Fig. 3 shows the dependence of the logarithm of capacity ratio (log k') of transition metal ions on the logarithm of the concentration of maleic acid. Maleic acid has a relatively weak complexing ability and buffering property in the studied pH range. As shown in Fig. 3 the retention of metal decreased in order IDA-silica > TSK Gel Chelate 5PW > Phthalein Purple column. The elution order of transition metal ions

$$Mn < Co < Cd < Zn < Ni < Pb < UO_2 < Cu$$

was the same for IDA-silica and TSK Gel Chelate 5PW columns and was in a good agreement with data published for other IDA-chelating cation- exchange resins such as Chelex 20 (BioRad) and MetPac CC-1 (Dionex).[13,14] A worse separation selectivity of the Zn/Cd pair, but better separation selectivity for the

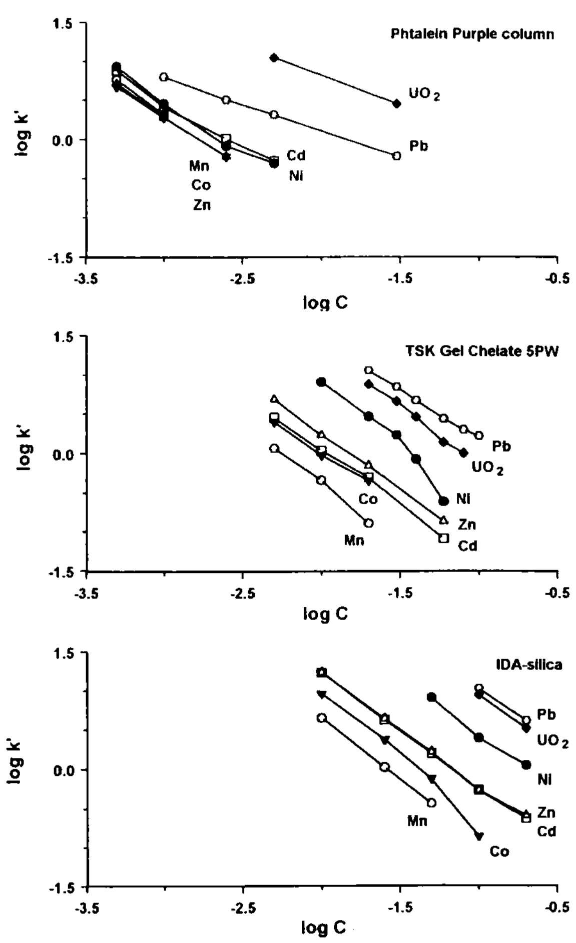

Figure 3. Dependence of the retention of transition metal ions on the concentration of maleic acid.

pair Cd/Co was obtained for the silica based column. A relatively low separation selectivity and different elution order were demonstrated for Phthalein Purple column. This difference in elution order can also be connected with the weaker complexing ability of the immobilised dye in comparison with maleic acid used as the eluent. It should be noted that the Tosoh TSK-Gel Chelate 5PW column retained the ions of nickel (II), copper (II), lead (II) and uranyl in maleic acid based eluents using a pH lower than the

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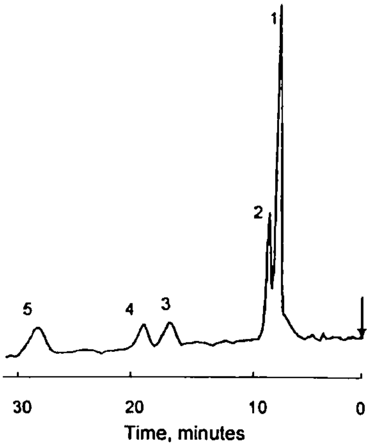

Figure 4. Separation of transition metals. Stationary phase, TSK Gel Chelate 5PW; mobile phase, 0.01 M tartaric acid; flowrate, 0.8 mL/min; photometric detection (490 nm, 0.3 aufs), derivatization with PAR-Zn-EDTA reagent at 1 mL/min flowrate. Sample: 10 μL of standard solution containing (1) 12 ppm Mg^{2+}; (2) 5 ppm Mn^{2+}; (3) 5 ppm Co^{2+}; (4) 5 ppm Cd^{2+}; (5) 5 ppm Zn^{2+}.

Table 2

Capacity Factors (k') of Some Transition Metals on Different Columns in Tartaric Acid Eluents

Metals	Phtalein Purple 0.001M	TSK Gel Chelate 5PW 0.01M	IDA-Silica 0.1M
Mn(II)	2.21	1.35	2.27
Co(II)	2.29	3.85	3.50
Zn(II)	2.68	7.12	5.41
Cd(II)	3.03	4.44	7.15
Pb(II)	6.76	no elution	no elution
Cu(II)	no elution	no elution	no elution

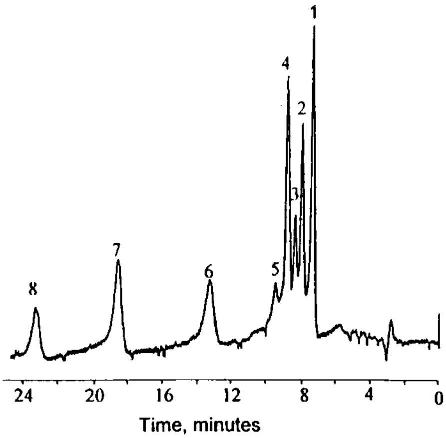

Figure 5. Separation of transition metals. Stationary phase, IDA-silica; mobile phase, 0.09 M tartaric acid; flowrate, 0.8 mL/min; photometric detection (490 nm, 0.2 aufs), derivatization with PAR-Zn-EDTA reagent at 1 mL/min flowrate. Sample: 100 µL of standard solution containing (1) 0.7 ppm Mg^{2+}; (2) 0.7 ppm Ca^{2+}; (3) 0.7 ppm Sr^{2+}; (4) 1.4 ppm Ba^{2+}; (5) 1.4 ppm Mn^{2+}; (6) 1.4 ppm Co^{2+}; (7) 1.4 ppm Cd^{2+}; (8) 1.4 ppm Zn^{2+}.

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stability range of the corresponding matrix. This leads to dissolution of the resin and strongly restricts the applicability of this column for the determination of the above mentioned metal ions.

One possible solution of this problem is the use of eluents containing a stronger complexant such as tartaric and oxalic acid. However, as shown in Table 2 the use of 0.01 M tartaric acid as eluent does not provide the elution of copper (II) and lead (II) from TSK Gel Chelate 5 PW column. Also, 0.1 M tartaric acid does not provide elution of these metals from the IDA silica column. It is interesting that the observed elution order for Zn(II) and Cd(II) is different for TSK Gel Chelate 5 PW and IDA-silica columns. The typical separations of alkaline earth and transition metal ions are presented in Fig. 4,5.

Fig. 6 shows the retention times of transition metal ions as function of pH in 0.02M oxalic acid eluent on TSK Gel Chelate 5 PW and IDA-silica columns. Using this eluent it was possible also to elute the strongly retained Cu(II) and In (III) from TSK Gel Chelate 5 PW over the whole of the studied pH range. At the same time little or no retention was observed for any of the transition metal ions except copper on the Phtalein Purple column. The observed retention order of the metal ions in oxalate eluent changed in comparison with maleic acid based eluent (Fig. 3). First of all, the weaker retention of UO_2^{2+} is

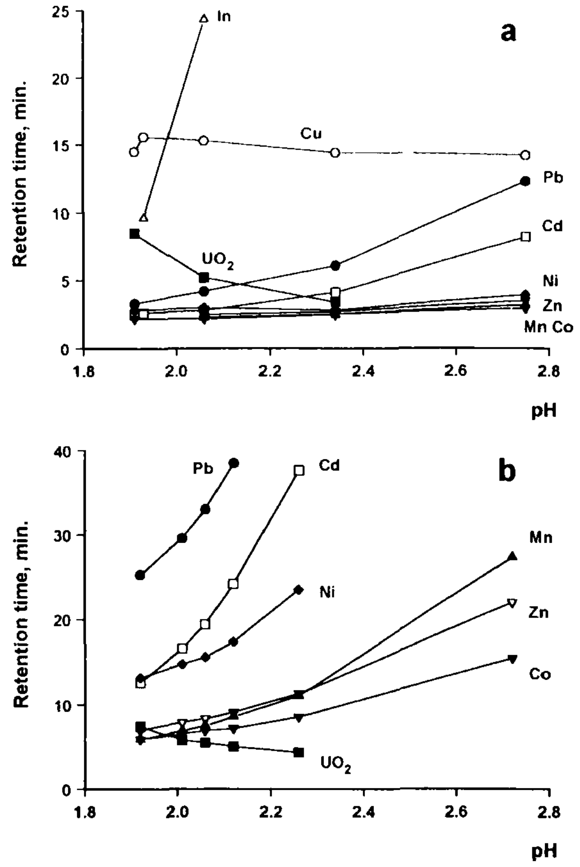

Figure 6. Influence of pH on retention times of transition metal ions in 0.02M oxalyc acid eluent. Stationary phases are (a) TSK Gel Chelate 5PW and (b) IDA-silica. Flow-rate, (a) 1 mL/min and (b) 0.8 mL/min.

connected with the higher stability of its oxalate complex. Secondly, the retention of manganese(II) and cadmium(II) was markedly increased relative to the other transition metal ions. Cadmium eluted after nickel and manganese eluted after zinc. Oxalate therefore improves the selectivity of separation for the pair Zn(II)/Cd(II) in the case of the IDA-silica and for the pair Cd(II)/Co(II) in the case of the TSK Gel Chelate 5 PW. More extensive mobile-phase complexation of separated metals occurred in oxalate eluents. Thus using 0.1 M oxalic acid the elution of strongly retained In(III) and Th^{4+} was obtained (Fig. 7).

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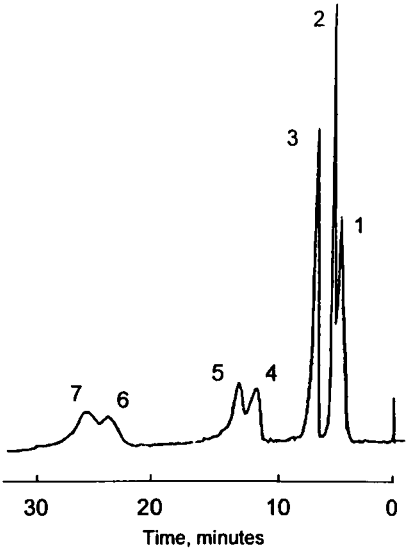

Figure 7. Separation of transition metals. Stationary phase, IDA-silica; mobile phase, 0.1 M oxalic acid; flowrate, 0.7 mL/min; photometric detection (490 nm, 0.2 aufs), derivatization with PAR-Zn-EDTA reagent at 1 mL/min flowrate. Sample: 100 μL of standard solution containing (1) impurities of alkaline-earth metal ions; (2) 0.8 ppm Co^{2+}; (3) 1.3 ppm Cd^{2+}; (4) 2.1 ppm Pb^{2+}; (5) 4.3 ppm UO^{2+};(6) 1.6 ppm In^{3+}; (7) 2.7 ppm Th^{4+}.

It should be mentioned that the feasibility of using tartaric and oxalic acid eluents is strongly restricted by the very low solubility of tartrates and especially of oxalates of alkaline-earth and transition metals. So, the injection onto chromatographic columns equilibrated with 0.01 M tartaric/oxalic acid of the sample solution containing at least 20 ppm one of each of magnesium, calcium, strontium and barium produced the splitting and distortion of chromatographic peaks and led to the marked decrease in efficiency of separation. Evidently, it takes place due to the formation of a precipitate of insoluble salts for a short time at the top of the column.

CONCLUSION

The comparison of different chelating ion-exchangers bearing iminodiacetic functionality confirmed the complexation in the stationary phase was the most important factor for retention of metal ions. Iminodiacetic acid bonded to silica showed the strongest retention of metal ions, and the Phthalein Purple coated column the weakest retention. Under the conditions studied the use of IDA silica and TSK Gel Chelate 5PW columns are of preference for the isocratic separation of transition metal ions. However, the applicability of the latter column is restricted by dissolution in acid media. So strong complexing eluents must be used for complete regeneration and elution of strongly retained copper(II) and iron (III). The solubility of the complexes of alkaline earth and transition metals in some dicarboxylic acid solution may restrict the application of the studied chromatographic conditions to the analysis of samples containing elevated concentration of these metals.

ACKNOWLEDGEMENTS

The authors acknowledge The European Environmental Research Organisation (EERO), and the University of Plymouth for support of this work.

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Received September 27, 1995
Accepted October 20, 1995
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