

1. Maarek, J. M., Jarry, G., de Cosnac, B., Lansart, A. and Hung, B. M., *Ann. Biomed. Eng.*, 1984, **12**, 281-303.
2. Cheong, W. F., Prahl, S. A. and Welch, A.-J., *IEEE J. Quant. Electr.*, 1990, **17**, 2166-2184.
3. Van Gemert, M. J. C. and Welch, A. J., *IEEE Eng. Med. Biol.*, 1989, **10**, 10-13.
4. Goldman, L., *The Biomedical Laser Technology and Clinical Applications*, Springer, Berlin, 1981.
5. Jarry, G., Lefabure, J. P., Debrey, S. and Perez, J., *Med. Biol. Eng. Comput.*, 1993, **31**, 157-164.
6. Huang, D., Swanson, E. A., Lin, C. P., Schuman, J. S., Stinson, W. G., Chang, W. *et al.*, *Science*, 1991, **254**, 1178-1181.
7. Anderson-Engels, S., Berg, R. and Svanberg, S., *Op. Lett.*, 1990, **15**, 1179-1181.
8. Shanthi, S. and Singh, M., *Innov. Tech. Biol. Med.*, 1996, **17**, 443-451.
9. Cui, W. and Ostrander, L. E., *IEEE Trans. Biomed. Eng.*, 1992, **39**, 194-201.
10. Wilson, B. C. and Adam, G., *Med. Phys.*, 1983, **10**, 824-830.
11. Flock, S. T., Patterson, M. S., Wilson, B. C. and Wyman, D. R., *IEEE Trans Biomed. Eng.*, 1989, **36**, 1162-1168.
12. Schmitt, J. M., Mihm, F. G. and Meindl, J. D., *Ann. Biomed. Eng.*, 1986, **14**, 35-52.
13. Susamma, C., Shanthi, S. and Singh, M., *Med. Biol. Eng. Comput.*, (submitted).
14. Wilson, B. C. and Jacques, S. L., *IEEE J. Quant. Electr.*, 1990, **26**, 2186-2199.
15. Shanthi, S. and Singh, M., *Med. Biol. Eng. Comput.*, 1997, **35**, 253-258.
16. Farrell, T. J. and Patterson, M. S., *Med. Phys.*, 1992, **19**, 879-888.
17. Jarry, G., Poupinel, L., Watson, J. and Lepine, T., *Appl. Opt.*, 1995, **34**, 2045-2054.
18. Parsa, P., Jacques, S. L. and Nishioka, N. S., *Appl. Opt.*, 1989, **28**, 2325-2330.
19. Singh, M., Kumaravel, M. and Namasivayam, A., *IETE Tech Rev.*, 1997, **12**, 195-200.

ACKNOWLEDGEMENT. We thank Ms S. Shnathi for carrying out the experiments.

Received 24 June 1997; revised accepted 17 October 1997

Microwave dissolution techniques for the analysis of geological materials by ICP-MS

V. Balaram

National Geophysical Research Institute, Hyderabad 500 007, India

Microwave ovens are being used increasingly for the dissolution of wide range of geological materials. Such devices are more useful especially in conjunction with high sensitive multi-element techniques such as inductively coupled plasma mass spectrometry (ICP-MS). This study evaluates the data of several trace and ultra-trace elements including specialized groups of elements such as rare earths, and platinum group elements and gold in a variety of rock and ore

samples after the samples were subjected to microwave digestion followed by ICP-MS analysis. Microwave digestion yielded very clear solutions rapidly. Data with reasonable precision and accuracy were obtained even for elements such as Zr, Hf, Nb and W the quantitative recoveries of which are very difficult to obtain using conventional open acid decompositions. Near-quantitative recoveries were obtained for Pt, Pd, Ag and Au even in difficult to dissolve 'chromite ore' samples. The gold values obtained on 10 g quantities of several field samples, and few international gold reference samples demonstrated the utility of microwave dissolutions in combination with ICP-MS in gold exploration studies.

MODERN geochemical studies involving both pure and applied aspects require geochemical data of several trace elements including specialized groups of elements such as rare earth elements (REE), large-ion-lithophile elements (LILE, e.g. Rb and Cs), high field strength elements (HFSE, e.g. Ta, Nb, Hf and Zr), platinum group elements (PGE) and gold in rocks ores and mineral samples with greater precision and accuracy at natural abundance levels. Analytical instrumental techniques such as atomic absorption spectrometry (both flame and flameless)¹, inductively coupled plasma atomic emission spectrometry² and inductively coupled plasma mass spectrometry³, are widely used to determine the major, minor, trace, and ultra-trace elements in rocks, ores and other geological samples. Most of the analytical techniques require samples in the form of solution for analysis. Though, there is growing interest in the atomic spectroscopic determination of elements directly in solid samples (powders) without the need of decomposition⁴, these methods have not gained popularity and are not suitable for routine application for several reasons. For example, solid sampling approaches in flame AAS are not directly utilizable because of insufficient dissociation of solid particles in the relatively cold flame⁵. The solid sampling approaches are particularly difficult in ICP-spectrometry because of physical and chemical interferences due to difference in transport and dissociation phenomena between the solid slurried samples and solutions used for calibration.

Despite significant progresses observed recently in analytical instrumentation, especially multi-element techniques⁶, sample preparation of geological samples continues to be a major problem because of the refractory nature of some of them. Sample preparation and development of methods have also become a growing field along with instrumental improvements⁷. Since the adaptation of a domestic oven for the dissolution of metal and mineral samples in a HCl-HF-HNO₃ medium⁸, there have been many attempts to use microwave heating systems to decompose various geological samples for precise estimation of major, minor, trace and ultra-trace elements including REE, using various instrumental

methods such as AAS⁹, ICP-AES and ICP-MS^{10,11}. In the present study, ICP-MS in combination with a microwave oven was examined for its potential for a rapid turnaround method for the analysis of a variety of geological samples for pure and applied geochemical studies.

The ICP-MS instrument used was a PlasmaQuad PQ1 (V.G. Elemental Analysis, UK) controlled by an IBM PC-XT micro computer and associated software (issue 3.1). More details are given elsewhere¹².

All the dissolutions were done using a computer controlled Model Qwave 3000 Microwave Oven (Ques-

tron Corporation, Mercerville, New Jersey, USA) with fume exhaust, rotating carousel with 10 multi-ply 120 ml PFA (tetrafluoroethylene-perfluoroalkoxy-ethylene) high pressure digestion vessels capable of operation up to 625 psi at 230°C. These vessels use microwave energy to rapidly heat the sample and thus enable more effective acid attack on refractory materials. The maximum pressure possible depends upon the nature of the material. This unit has a pressure monitor system with feedback to enable computer control of the pressure and temperature within the vessels. In general, about 900 W magnetron power was used for the digestions with microwave

Table 1. Concentrations ($\mu\text{g/g}$) of several trace and ultra-trace elements including rare earths in a few geological references samples determined by ICP-MS after microwave digestion

Element	G-2 (Granite)		W-2 (Diabase)		JB-2 (Basalt)		MRG-1 (Gabbro)	
	ICP-MS value*	Certified value ¹⁷	ICP-MS value*	Certified value ¹⁷	ICP-MS value*	Certified value ¹⁷	ICP-MS value*	Certified value ¹⁷
Li	30.28	34.0	10.01	9.3	8.37	8.0	3.83	4.2
Be	2.44	2.5	1.28	1.3	0.26	0.27	0.51	0.61
Sc	2.68	3.5	34.61	35.0	52.63	54.4	52.44	55.0
V	38.12	36.0	251.16	262.0	550.7	578.0	517.88	526.0
Cr	9.41	8.7	92.19	93.0	27.33	27.4	420.89	430.0
Co	4.76	4.6	43.46	44.0	37.32	39.8	87.25	87.0
Ni	4.72	5.0	69.84	70.0	15.08	14.2	188.55	193.0
Cu	12.11	11.0	100.17	103.0	210.0	227.0	120.45	134.0
Zn	88.75	86.0	79.27	77.0	116.33	110.0	179.63	191.0
Ga	22.55	23.0	18.44	20.0	17.28	17.0	18.19	17.0
Ge	0.93	1.14	1.10	1.0	1.30	1.28	0.28	—
Rb	166.01	170.0	21.22	20.0	6.34	6.2	8.59	8.5
Sr	476.33	478.0	198.61	194.0	182.76	178.0	269.95	266.0
Y	10.70	11.0	25.03	24.0	25.75	24.9	14.50	14.0
Zr	301.19	309.0	100.09	94.0	51.73	51.4	101.42	108.0
Nb	12.17	12.0	7.80	7.9	0.76	0.90	19.41	20.0
Mo	6.94	1.02	0.62	0.6	0.96	1.1	0.91	0.87
Cd	0.02	0.016	0.09	0.104	0.12	0.14	0.15	0.168
In	0.04	0.032	0.09	—	0.05	0.067	2.94	—
Sn	2.01	1.8	3.11	—	0.60	0.56	3.51	3.6
Sb	0.09	0.07	0.71	0.79	0.25	0.27	0.84	0.86
Cs	1.29	1.34	0.96	0.99	0.86	0.90	0.61	0.57
Ba	1824.92	1882.0	179.79	182.0	215.44	208.0	54.34	61.0
La	88.44	89.0	11.12	11.4	2.49	2.37	9.71	9.8
Ce	157.76	160.0	23.50	24.0	6.66	6.77	25.95	26.0
Pr	16.38	18.0	2.90	5.9	1.04	0.94	3.52	3.4
Nd	55.45	55.0	13.26	14.0	6.81	6.7	19.48	19.2
Sm	7.38	7.2	3.40	3.25	2.19	2.25	4.66	4.5
Eu	1.50	1.4	1.15	1.1	0.90	0.86	1.41	1.39
Gd	4.20	4.3	3.69	3.6	3.22	3.28	4.01	4.0
Tb	0.51	0.48	0.64	0.63	0.59	0.62	0.54	0.51
Dy	2.62	2.4	3.68	3.8	3.89	3.66	2.86	2.9
Ho	0.38	0.4	0.76	0.76	0.83	0.81	0.54	0.49
Er	0.97	0.92	2.35	2.5	2.68	2.63	1.18	1.12
Tm	0.16	0.18	0.35	0.38	0.45	0.45	0.13	0.11
Yb	0.75	0.80	2.10	2.05	2.78	2.51	0.63	0.60
Lu	0.11	0.11	0.31	0.33	0.40	0.39	0.12	0.12
Hf	7.69	7.9	2.56	2.56	1.42	1.42	3.89	3.72
Ta	0.92	0.88	0.53	0.50	0.18	0.20	0.78	0.8
W	0.39	—	0.31	0.30	0.30	0.26	0.32	0.30
Tl	0.98	0.91	0.18	0.2	0.94	—	0.05	—
Pb	31.82	30	10.01	9.3	5.68	5.4	9.51	10
Th	26.13	24.7	2.29	2.2	0.33	0.33	0.87	0.93
U	2.04	2.07	0.52	0.53	0.20	0.16	0.28	0.24

SY-2 (Syenite) was used for calibration; *Average of four determinations; G-2 & W-2 are from the US Geological Survey; JB-2 is from Geological Survey of Japan; SY-2 and MRG-1 are from Canadian Certified Reference Materials Project; Average precision < 5% RSD; — not available.

power duration time of 25 min. The maximum pressure and temperature attained during digestion were approximately 380 psi and 205°C. All the samples gave clear solutions. All the samples were dissolved in duplicate and each sample analysed twice.

Here, some of the results of the studies carried out in our laboratory using microwave digestion, of rock and ore samples and subsequent estimation of number of trace elements including specialized groups such as rare earths, platinum group elements, by ICP-MS are presented.

For the estimation of rare earths and several other trace elements, 100 mg quantities of different geochemical reference samples (SY-2, G-2, W-2, JB-2 and MRG-1) were dissolved in a PFA vessel utilizing a mixed acid attack of HF-HNO₃-HClO₄ (7 ml + 3 ml + 1 ml) after adding 1 ml of 10 µg/ml Rh and Bi to act as internal standards. The vessels were cooled under tap water to room temperature before opening the lids. Solutions were inspected visually, and the microwave program was repeated until the samples completely dissolved. For consistency, however each material was processed

through the microwave program three times. After microwave digestion, the contents were transferred to 100 ml teflon beakers, silica was expelled by heating at 210°C on a hotplate. The residue was dissolved in 20 ml of 1:1 HNO₃. The contents were cooled and the volume made up to 100 ml and stored in polyethylene bottles. The ICP-MS analysis for REE and several trace elements was carried out as described elsewhere¹³ and the results are presented in Table 1.

Estimation of gold concentrations was carried out in a few Chinese gold reference samples (GAu-8 to GAu-18). To 2 g sample in all PFA-microwave digestion vessel, 10 ml of freshly prepared aqua regia, 5 ml bromine, 10 ml of HF, 1 ml of HClO₄ and 5 ml of 10 µg/ml Rh (to act as an internal standard) were added. The samples were digested using microwave oven at a maximum pressure of 625 psi and a temperature of 210°C for 30 min. The microwave program was repeated once more with 20 min interval. After cooling, the contents in the respective digestion vessels were transferred to teflon beakers. Silica was expelled by heating the beakers on hotplate (220°C) and the contents were reduced to about 10 ml by further heating and the final solution brought to 500 ml volume with double distilled water before the estimation of gold by ICP-MS¹⁴. The results are presented in Table 2.

Standard reference materials, noble metal-bearing nickel-copper matte (PTM-1), and chromite ores (CHR-Pt* and CHR-Bkg) were chosen for this purpose. 0.5 g sub-sample was weighed in each case into a PFA-microwave digestion vessel, 5 ml of aqua regia, 3 ml of HF and 2 ml HClO₄ were added. Later 1 ml of 10 µg/ml cesium was added to act as an internal standard. The samples were digested in a microwave oven with a 30 min microwave program. The program was repeated once more with a time interval of 20 min cooling time in between. After cooling to room temperature under tap water, the samples were transferred to 100 ml teflon beakers and the contents were evaporated to incipient dryness at 220°C on hotplate. The residue was dissolved

Table 2. Concentrations of gold in Chinese gold reference samples determined by ICP-MS after microwave digestion of samples (total dissolution using HF)

Sample	Au	
	ICP-MS value*	Certified value ¹⁶
GAu-8	7.0 ng/g	0.5 ng/g
GAu-9	10.0 ng/g	1.5 ng/g
GAu-10	15.0 ng/g	5.3 ng/g
GAu-11	17.0 ng/g	14.3 ng/g
GAu-12	25.0 ng/g	21.5 ng/g
GAu-13	61.0 ng/g	50.0 ng/g
GAu-14	0.12 µg/g	0.10 µg/g
GAu-15	0.32 µg/g	0.30 µg/g
GAu-16	1.08 µg/g	1.09 µg/g
GAu-17	3.30 µg/g	3.40 µg/g
GAu-18	10.09 µg/g	10.00 µg/g

*Average of four determinations.
Average precisions < 10% RSD.

Table 3. Concentrations (µg/g) of precious metals determined by ICP-MS after the precious metal reference samples dissolved by the microwave digestion procedure

Element	PTM-1		CHR-Pt*		CHR-Bkg	
	ICP-MS value*	Certified value ¹⁷	ICP-MS value*	Certified value ¹⁷	ICP-MS value*	Certified value ¹⁷
Ru	0.34	0.5	0.80	9.2	0.07	0.067
Rh	0.94	0.9	1.00	4.70	0.03	0.009
Pd	7.89	8.1	83.13	80.8	0.11	0.07
Ag	65.80	66.0	23.24	—	20.06	—
Os	0.11	0.14	0.89	1.9	0.03	0.027
Ir	0.40	0.3	1.25	6.2	0.71	1.028
Pt	5.75	5.8	58.01	58.0	0.10	0.05
Au	1.70	1.8	4.51	4.3	0.04	0.028

*Average of four determinations.
Average precisions < 10% RSD.

by the addition of 20 ml of 1:1 HNO₃ and heating. The contents were cooled and the volume made to 100 ml with double distilled water. The solutions were analysed for Au, Ag and PGE using ICP-MS¹⁵ and the results are presented in Table 3.

It is well known that gold occurs at very low concentrations and is distributed heterogeneously in rocks and minerals. Consequently, relatively large sample sizes (> 10 g) are typically processed to obtain representative concentrations. Gold was extracted from 10 g sample in some field samples from Karnataka and a few international gold reference samples using microwave digestion after the sample was attacked by aqua regia by the following microwave dissolution procedure. 10 g sample (260 mesh) was taken in a porcelain crucible and roasted for 30 min in a muffle furnace at 700°C. After cooling, the sample was transferred to 125 ml PFA-microwave digestion vessel and 30 ml of freshly prepared aqua regia was added. All the samples were digested in a microwave oven for 20 min. The microwave program was repeated once more to get maximum extraction of gold from the samples. After cooling the vessels to room temperature, the contents in each case were transferred to a 250 ml volumetric flask and the volume was made. The solutions were filtered using Whatman 41 filter paper, 10 ml of the filtrate was diluted to 100 ml after adding 1 ml of 10 µg/ml Rh to act as an internal standard. This will enable to keep the total dissolved solids (TDS) below 0.4% as ICP-MS cannot tolerate higher TDS levels. Some of the field samples (10 g each) were also digested using normal open digestion procedure in a 250 ml Corning glass beaker, after adding 50 ml of freshly prepared aqua regia. Heating (at 210°C) was done for 5–6 h under reflux conditions by keeping the volume of aqua regia constant at 50 ml by periodic addition. Finally, the volume was made to 250 ml. The filtration, addition of internal standard, and dilution for a working solution were done exactly in the same way as in the case of closed microwave digestion procedure. The samples in the case of both closed microwave and open digestion were analysed by ICP-MS¹⁴ and results are presented in Tables 4 and 5.

Data presented (Table 1) for a series of four geological reference samples covering a wide spectrum of reference rock samples, show that data obtained for the rare earths and several other trace elements show reasonable agreement with certified values with precisions < 5% relative standard deviation (RSD) and a comparable accuracy for most of the elements. Especially the data for Ni, Zr, Nb, Ta, Hf and W the quantitative extractions of which are very difficult using conventional dissolution procedures, show almost quantitative recoveries using microwave dissolution.

The values of gold (Table 2) ranging from ng/g to µg/g obtained after the microwave dissolution followed

by ICP-MS estimation show good agreement with certified values except in cases where gold is present at ultra-trace levels (< 5 ng/g). On the other hand, Table 3 shows the effectiveness and utility of microwave digestion of 'difficult to dissolve' samples such as chromites for subsequent estimation of gold, silver and other precious metals by very high sensitive technique such as ICP-MS. These results also show that the measured values are generally well within the range of reference values for certain elements such as Ag, Au, Pt and Pd in all the samples. For other elements like Os, Ir, agreement is good only in the case of PTM-1 and CHK-Bkg in which the concentrations of these elements are low. In the case of CHR-Pt* low recoveries were obtained for Ru, Rh and Ir, suggesting that some more detailed studies are required.

The microwave digestion of 10 g samples followed by the determination of gold using ICP-MS was examined for its potential for use in gold exploration studies. The concentrations of gold obtained in some international gold reference samples and one field sample from Karnataka are presented in Table 4. The per cent recoveries

Table 4. Concentration of gold (µg/g) obtained by ICP-MS in different gold reference materials after 10 g samples subjected to microwave dissolution in comparison with certified values wherever available (partial dissolution using aqua regia only)

Sample	Au (µg/g)		
	ICP-MS value*	Reference value ¹⁶	Recovery of Au (%)
GAu-15	0.12	0.30	73.33
GAu-16	0.81	1.09	74.31
GAu-17	2.91	3.40	85.59
GAu-18	9.46	10.00	94.60
Aj Ore	7.89	9.31 [†]	84.75
PTM-1	1.81	1.80 [†]	100.00

*NGRI value.

*Average of four determinations.

Average precision < 8% RSD.

[†]W. S. Bowman, CANMET Certified Reference Materials, CCRMP 90-IE (1990).

Table 5. Comparison of the effectiveness of microwave digestion with conventional open digestion in the extraction of gold from a few gold ore samples from Karnataka

Sample	Values of gold (µg/g) determined by ICP-MS after microwave dissolution*	10 g sample was digested Open digestion*
GRS 17	0.57	0.19
TKG 2132	1.56	0.39
TKG 232	0.86	0.39
TKG 233	0.73	0.22
TKG 247	0.66	0.32
TKG 278	0.74	0.21

*Average of four determinations.

Average precision < 8% RSD.

of gold obtained for different samples ranged between 73 and 100. These results suggest that the microwave digestion of rock and ore samples followed by the estimation of gold by ICP-MS can be extremely useful in gold exploration studies.

In an attempt to compare the high efficiency of microwave digestion method with conventional open digestion method for the extraction of gold, a few iron formation samples from Karnataka were dissolved using both the procedures and gold concentrations were estimated by ICP-MS. The comparative results (Table 5) suggest that microwave digestion procedure is more rapid and efficient.

In general, the detection limits obtained for different elements in this study were less than 0.05 ng/ml (ppb) for all the elements, and the average value obtained on replicate analyses of different samples in these investigations are within 5% RSD for all the trace elements including REE, and within 10% RSD for PGE and gold.

The digestion of geological samples using microwave decomposition methods is simple and can be completed within minutes. On the other hand, conventional methods of open acid digestions and fusion methods require few hours or days to completion. As an added advantage, exposure to hazardous chemicals and poisonous fumes is considerably reduced. The other advantages of microwave dissolution include yielding very low blank levels, use of relatively small amounts of acids and other reagents apart from allowing very fast dissolutions. Extremely low levels of detection limits (in the range of ppb and ppt) are obtained for several elements because of low blank levels obtained in these studies. So the combination of microwave oven for sample dissolution and ICP-MS for element detection and estimation would enable us to generate geoanalytical data of several trace elements including specialized groups such as rare earths, platinum group elements and gold with greater precision

and accuracy at natural abundance levels than were previously achievable.

1. Viets, J. G. and O'Leary, R. M., *J. Geochem. Explor.*, 1992, **44**, 107-138
2. Jarvis, I. and Jarvis, K. E., *Chem. Geol.*, 1992, **95**, 1-33
3. Balaram, V., *Trends Anal. Chem.*, 1996, **15**, 475-486
4. Voellkopf, U., Paul, M. and Denoyer, E. R., *Fresenius J. Anal. Chem.*, 1992, **342**, 917-923.
5. Hoenig, M. and Kersabiec, A. M., *Spectrochim. Acta, Part B*, 1996, **51**, 1297-1307.
6. Brenner, I. B. and Zander, A., *Fresenius J. Anal. Chem.*, 1996, **355**, 559-570.
7. Chao, T. and Sanzolone, R. F., *J. Geochem. Explor.*, 1992, **44**, 65-106.
8. Mathese, S. A., Farrell, R. F. and Mackie, A. J., *Tech. Prog. Rep. US Bur. Mines*, 1983, **120**, 9-18.
9. Suzuki, T. and Sensui, M., *Anal. Chim. Acta*, 1991, **245**, 43-48.
10. Totland, M. M., Jarivis, I. and Jarvis, K. E., *Chem. Geol.*, 1992, **95**, 35-62.
11. Sengupta, J. G. and Bertrand, N. B., *Talanta*, 1995, **42**, 1595-1607.
12. Balaram, V., Ramesh, S. L. and Anjaiah, K. V., *Fresenius J. Anal. Chem.*, 1995, **353**, 176-182.
13. Balaram, V., Ramesh, S. L. and Anjaiah, K. V., *Geostand. Newslett.*, 1996, **20**, 71-78.
14. Balaram, V. and Anjaiah, K. V., *Indian J. Chem. Soc.*, 1997, **74**, 581-583.
15. Balaram, V., Hussain, S. M., Uday Raj, B., Charan, S. N., Subba Rao, D. V., Anjaiah, K. V., Ramesh, S. L. and Ilangovan, S., *Atom. Spectrosc.*, 1997, **18**, 17-22.
16. Mingcai, Y., Chunshu, W., Qunxian, C., Tiexin, G. and Qinghua, C., *Geostand. Newslett.*, 1995, **19**, 125-133.
17. Govindaraju, K., *Geostand. Newslett.*, 1994, **18**, 1-158.

ACKNOWLEDGEMENTS. I am grateful to Dr H. K. Gupta, Director, National Geophysical Research Institute, Hyderabad, for his kind permission to publish this paper. I also thank Dr S. M. Naqvi, for his valuable advice and constant encouragement. Dr S. Nirmal Charan is thanked for helpful suggestions and critical reading of the manuscript. I am grateful to M/s Shiva Chem Technology Pvt Ltd, Hyderabad for making their Microwave Digestion System available for these studies.

Received 25 August 1997; revised accepted 15 October 1997

Erratum

Surjit Singh – An obituary

[*Curr. Sci.*, 1997, **73**, 892]

Read '12 June 1940' instead of '12 June 1994' in 3rd column, 2 paragraph, 13th line.