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ROLE OF GRAPHITIC CARBON PARTICLES IN RADIATIVE TRANSFER IN THE ARCTIC HAZE*

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ABSTRACT

Large concentrations of combustion-generated graphitic carbon particles have been identified at ground level and at altitude in the Arctic atmosphere. Concentrations of these particles during certain times of year and at certain altitudes are comparable to those in urban centers in the United States. These graphitic particles, which have a structure similar to carbon black, have been identified on a molecular level using Raman spectroscopy at sites in the Alaskan, Canadian, and Norwegian Arctic. The black particles are very effective absorbers of solar radiation and can lead to significant heating effects, depending primarily on their distribution in time and space. Recent measurements from an airplane indicate that high concentrations of graphitic particles occur throughout the Arctic troposphere, and at certain altitudes the concentrations can be significantly higher than at ground level. The implications of these results to radiative transfer will be discussed.

INTRODUCTION

Aerosol particles can change the radiation balance of the earth, leading to a cooling or heating effect with the magnitude and sign of the temperature change largely dependent on aerosol optical properties, aerosol concentrations, and the albedo of the underlying surface (ref.1). A purely scattering aerosol will reflect energy that would normally be absorbed by the earth-atmosphere system back to space and leads to a cooling effect. As one adds an absorbing component to the aerosol, it can lead to a heating of the earth-atmosphere system if the reflectivity of the underlying surface is sufficiently high. Most studies of the effects of aerosols on atmospheric radiative transfer on a global scale have assumed a dominantly scattering aerosol with only a small absorbing component, since this appears to be a good representation of naturally occurring aerosols.

Analysis of the optical properties of aerosols in urban locations, however, indicates that the absorbing component can be substantial, due to the presence of large concentrations of combustion-generated graphitic carbon particles that have been identified on a molecular level by Raman spectroscopy (refs. 2-4). If these particles can be transported on a global scale, then one would expect to

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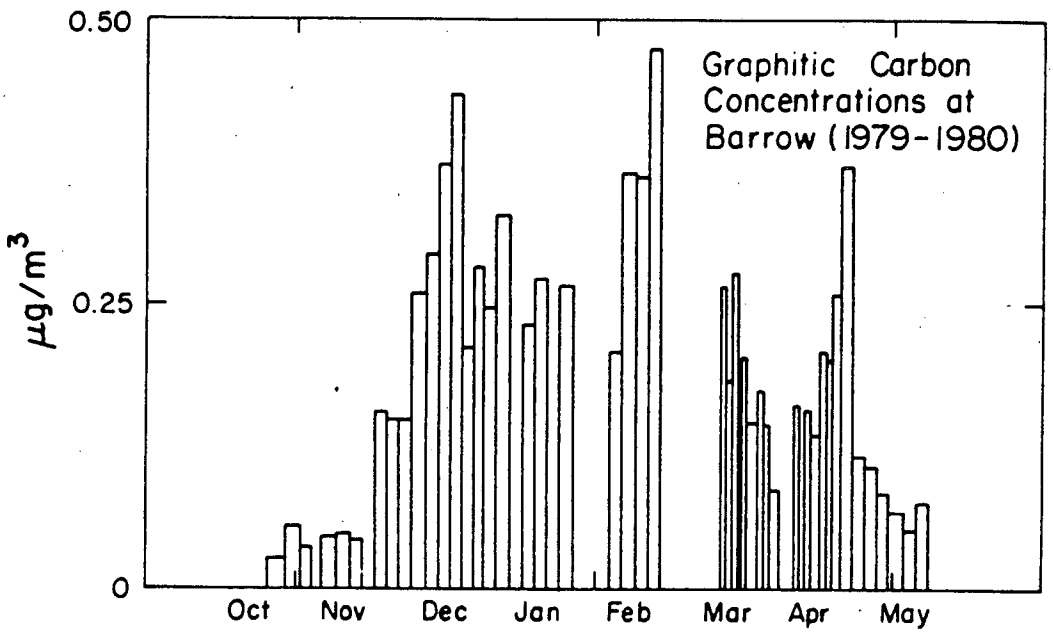
observe significant aerosol absorption even in remote locations such as the Arctic region. In this paper, we report on the observation of substantial concentrations of graphitic carbon particles at ground level and at altitude in the western Arctic. The concentrations of these particles appear to be sufficiently large to lead to significant heating effects during springtime over the high surface albedo polar icecap.

GROUND-LEVEL CONCENTRATIONS OF GRAPHITIC PARTICLES IN THE WESTERN ARCTIC

Recent studies at ground level in the Alaskan Arctic (refs.5-7) show the presence of substantial concentrations of carbon- and sulfur-containing particles that seem to be characteristic of the Arctic region as a whole (refs.8-10). These particles are effective scatterers and absorbers of visible radiation (refs.7,11) and appear to be responsible for the phenomenon of Arctic haze first reported by Mitchell (ref.12). On the basis of trace element analysis, it has been suggested that these particles originate from anthropogenic sources at mid-latitudes (refs.5,8). Direct substantiation of combustion-generated particles in the Arctic atmosphere has been provided by the identification of large concentrations of graphitic carbon particles at the GMCC-NOAA observatory near Barrow, Alaska (ref.7). The concentrations of these particles during winter and spring are only about a factor of 4 less than typical urban concentrations in the United States (ref.7), as shown in Fig. 1. These graphitic particles, which can only be produced from high-temperature combustion processes, have been identified on a molecular level using Raman spectroscopy. If one excludes natural burning processes that are not expected to be a significant source term during winter and spring when the Arctic haze is at a maximum, then one can attribute these graphitic particles directly to anthropogenic activities. These particles, which have large absorption cross sections ($\sim 10\ m^2/g$) in the solar spectral region, can lead to significant heating effects (refs.13-15). The magnitude of these effects largely depends on the vertical and horizontal distributions of the graphitic particles as well as their concentrations as a function of time of year (refs.14,15). In this paper, we report on an extension of our studies of carbon particles in the Alaskan Arctic to the Canadian and the Norwegian Arctic. These studies, using the Raman scattering technique, identify substantial concentrations of graphitic carbon particles at ground-level stations throughout the western Arctic.

The Raman spectra are obtained directly from aerosol particles collected on various filter media without any pretreatment procedures. These spectra are observed on top of a large fluorescent background, which is due both to the filter media and the highly fluorescent material in the sample. Irradiation of the sample with the argon laser for 24 hours reduced this background by about an order of magnitude. The intensity of the Raman spectra was typically about 1%



Average Graphitic Carbon Concentration in Urban Areas

Argonne, Illinois	1.8 $\mu g/m^3$
Gaithersburg, Maryland	1.3 $\mu g/m^3$
Denver, Colorado	1.6 $\mu g/m^3$
Anaheim, California	3.2 $\mu g/m^3$
Fremont, California	2.2 $\mu g/m^3$
Berkeley, California	1.3 $\mu g/m^3$
New York, New York	4.3 $\mu g/m^3$

Fig. 1. Seasonal variation in graphitic carbon concentration at Barrow, Alaska (1979-80). Shown for comparison are average concentrations at various urban sites in the United States.

of the fluorescent background. Aerosol samples were obtained from six Arctic sites: Barrow in the Alaskan Arctic; Mould Bay, Igloolik, and Alert in the Canadian Arctic; and Bear Island and Spitzbergen in the Norwegian Arctic. The samples from the Alaskan Arctic were collected on prefired quartz-fiber filters (Pallflex 2500 QAO) with a sampler installed at the NOAA-GMCC observatory in cooperation with B.A. Bodhaine of the GMCC program. The samples from the Canadian and Norwegian Arctic were collected on Whatman 41 filters and were provided respectively by L.A. Barrie of the Canadian Atmospheric Environment Service and B. Ottar of the Norwegian Institute for Arctic Research.

Raman scattering and infrared absorption spectroscopy are complementary techniques that measure the vibrational spectra of gases, liquids, and solids. Often vibrational modes that are infrared inactive are Raman active and vice versa. Graphitic structures in which trivalent carbon atoms occupy lattice

sites in a two-dimensional hexagonal honeycomb network have intense Raman modes but very weak infrared vibrational spectra. These Raman modes, which were first observed by Tuinstra and Koenig (ref.16), enable the identification of graphitic structures even in the presence of a complex mixture of substances. Solvent extraction, heat treatment, optical absorption, and morphology studies (ref.17) can provide indirect evidence for a graphitic component; but Raman spectroscopy appears to be the only presently available method for making unambiguous identifications on a molecular level.

The Raman scattering technique has been applied to identify substantial concentrations of graphitic particles in combustion effluents, urban air (refs.2,3), and the Alaskan Arctic (ref.7). The spectra from these samples show the presence of two Raman modes located at $\sim$ 1350 cm^{-1} and 1600 cm^{-1} that have been identified as due to phonons propagating with graphitic planes (ref.16). In Fig. 2 these measurements are extended to samples collected from three sites in the Canadian Arctic (Mould Bay, Igloolik, Alert) and two sites in the Norwegian Arctic (Spitzbergen, Bear Island). All samples were collected at similar times of year; but due to sample availability, some samples are from 1980 and others from 1981. It is clear from the spectra that all sites show the presence of significant concentrations of graphitic particles. There are some differences in the relative intensities and line shapes of the two Raman modes, but these could be due to systematic errors in fluorescence subtraction for the 1350 cm^{-1} mode, which is located on a highly sloping background. If one assumes fixed optical constants (Raman cross sections, absorption cross sections), one can use the integrated intensity of the 1600 cm^{-1} Raman mode as a measure of the relative concentrations of graphitic particles at these sites. These analyses indicate that the concentrations at all these sites are quite comparable with the largest and smallest within about a factor of 3 from each other. The relative ordering of these concentrations for Spitzbergen, Bear Island, Barrow, Mould Bay, Alert, and Igloolik are 2.1/1.7/1/0.8/0.8/0.7. It should be emphasized that this analysis is for a particular time interval, and the relative contributions could vary considerably from one time period to the next. In summary, these results show that the large concentrations of graphitic particles found at the Barrow, Alaska, site are not a local phenomenon but are characteristic of ground-level stations across the western Arctic.

VERTICAL DISTRIBUTION OF GRAPHITIC PARTICLES IN THE NORWEGIAN ARCTIC

If the large concentrations of graphitic particles found at ground-level stations also occur throughout the Arctic troposphere, then they could have a significant impact on the Arctic radiation and climate (refs.14,15). During March and April 1983, a series of flights (AGASP) organized by NOAA explored the vertical and horizontal distributions of the Arctic haze. One of the instruments

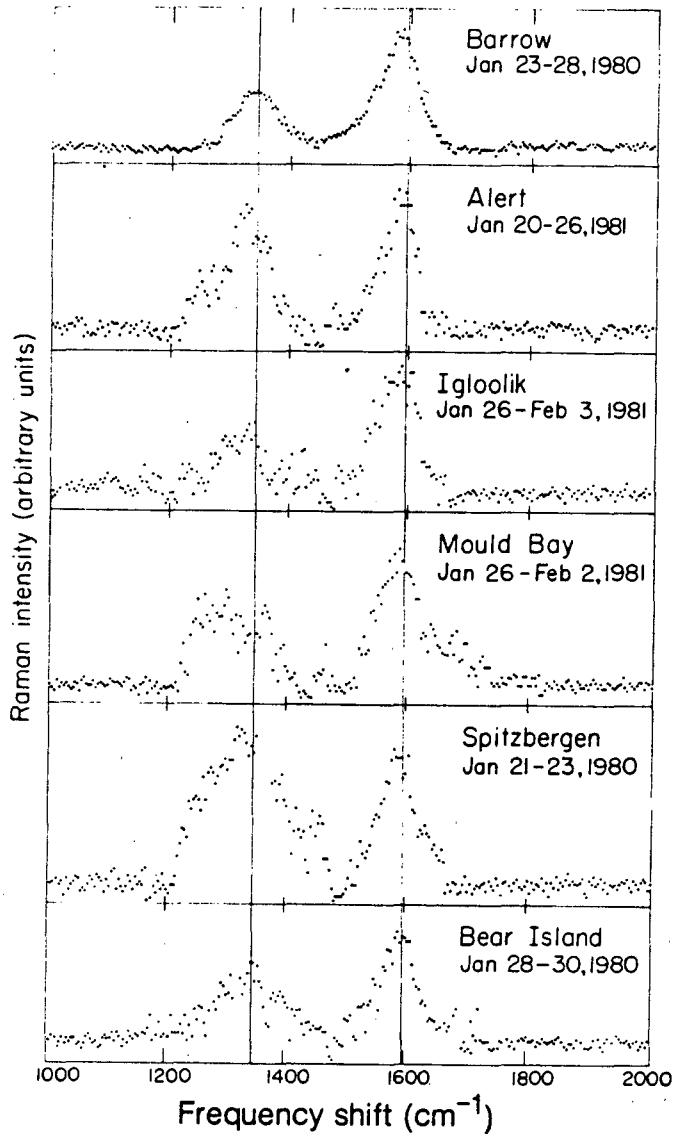


Fig. 2. Raman spectra of particles collected in the Alaskan Arctic (Barrow) compared with samples collected in the Canadian Arctic (Alert, Igloolik, Mould Bay) and the Norwegian Arctic (Spitzbergen, Bear Island).

on these flights was an aethalometer (ref.18)(soot-meter), which was developed at Lawrence Berkeley Laboratory and is described in detail in these proceedings by Hansen et al. This instrument has the capability of determining graphitic carbon concentrations on a real-time basis, using the calibration developed by Gundel et al. also described in these proceedings. The data from the flights have not yet been fully analyzed, but preliminary analysis of one of the flights in the Norwegian Arctic has been completed. The flight originated in Bodo, Norway, on March 31, 1983, at ∿ 8:30 a.m. The flight was essentially in a northerly direction over Bear Island to northern Spitzbergen at 80° N, 15° E and then back to Bodo. The flight profile included a slow descent from 7 km to 0.1 km at 74° N, 25° E near Bear Island. This descent started at 10:30 a.m. and finished around noon. The graphitic carbon concentrations as a function of altitude are

shown for this descent in Fig. 3. Also shown for comparison are the average ground-level concentrations found in Barrow for April 1982 and the average ground-level concentrations found in various urban areas in the United States.

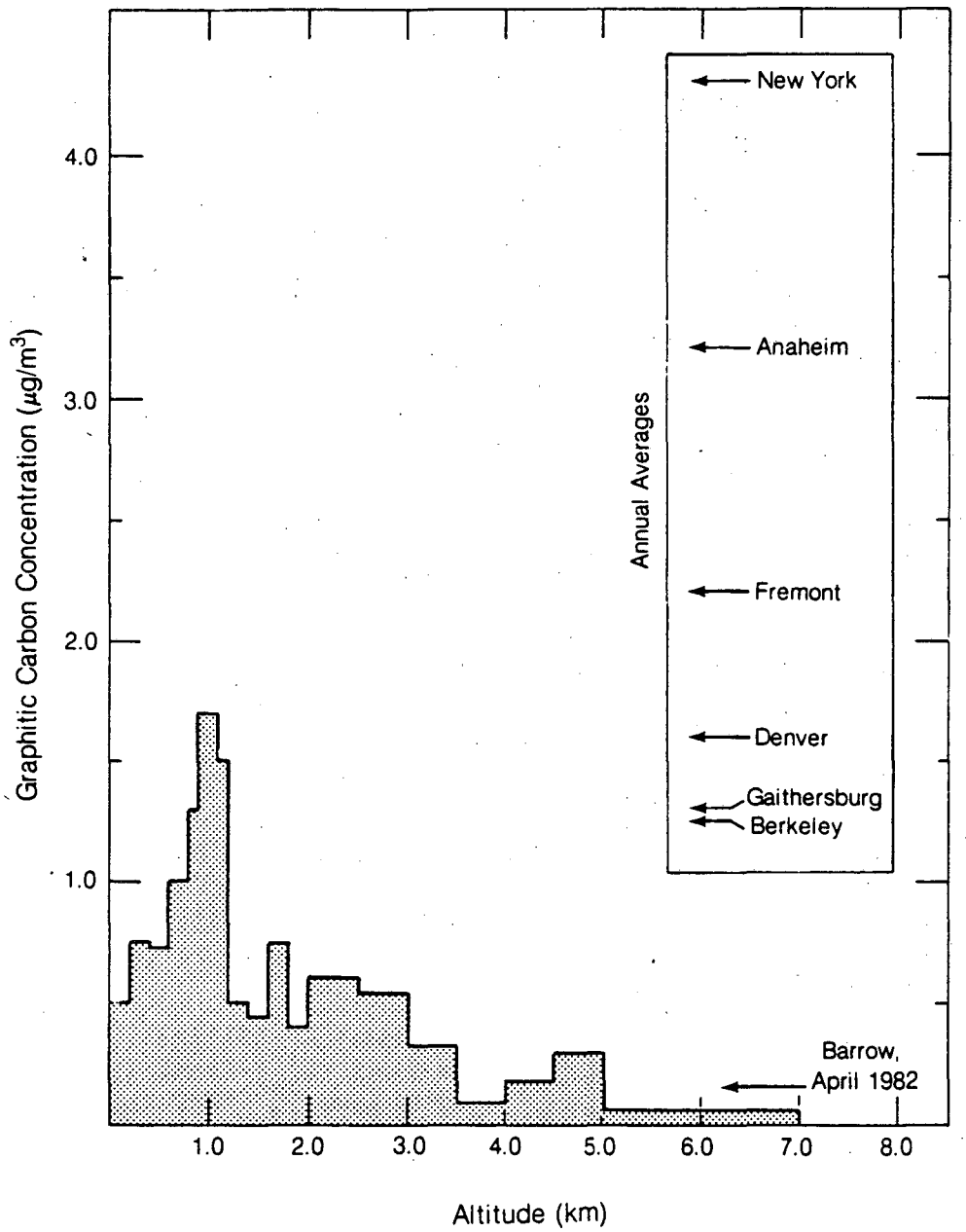


Fig. 3. Vertical profile of graphitic carbon concentration in the Norwegian Arctic on March 31, 1983, at ∿ 74° N, 25° E. Shown for comparison are the average April ground-level concentrations at the NOAA-GMCC observatory at Barrow, Alaska, and those at various urban locations in the United States.

It is clear from this figure that the vertical profile has considerable structure with at least three layers located at approximately 1 km, 2.5 km, and 4.5 km. The concentrations within these layers are large, with the peak concentrations at 1 km only about a factor of 2.5 lower than those in New York City and a

factor of 10 higher than the 0.15 $\mu g/m^3$ April 1982 ground-level concentrations at Barrow, Alaska. The flight profile also indicates a relatively clean region at low altitudes, which is consistent with the Barrow results at ground level and the limited ground-level measurements we've made in the Norwegian Arctic.

Recent modelling studies of the possible effects of the Arctic haze on the radiation budget of the Arctic indicate rather substantial changes in the heat balance if the optical depth due to absorption is sufficiently large (refs.14, 15). One can calculate this optical depth from the results shown in Fig. 3 for various models of the Arctic aerosol. In these models, it is important to distinguish between graphitic particles mixed internally or externally with the other nonabsorbing components. Such differences, as shown by Ackerman and Toon (ref.19), can lead to significant changes in aerosol absorption. We will consider three examples.

1. Graphitic carbon particles internally mixed with all the major submicron aerosol components (i.e., sulfates, organics).

2. Graphitic carbon particles internally mixed with only submicron organic aerosol components.

3. Graphitic carbon particles externally mixed with the other aerosol components.

Of these three, the first two are the most likely combinations. For these, we treat the particles as homogeneous spheres and mix in the various components by volume mixing of dielectric constants (ref.20). In these calculations the indices of refraction of graphitic carbon were chosen to be 1.94-0.66 i (ref.19), with a density of 1.5; and the index of refraction of the nonabsorbing components was taken to be 1.5. The relative concentrations of graphitic carbon, sulfates, and organic carbon are obtained from ground-level measurements in April at Barrow, Alaska, where detailed chemical analysis of the submicron aerosol has been completed. The particle size distribution for the submicron aerosol is assumed to be log-normal with $r_{gv} = 0.2\ \mu$ and $\sigma_g = 2$, which are obtained from Whitby (ref.21) for the urban aerosol and are consistent with the results of Heintzenberg (ref.10) for the Arctic aerosol. For the first two examples, Mie calculations yield absorption cross sections of 19 m^2 and 12 m^2 per gram of graphitic carbon, respectively. For the external mixture, we use the photoacoustic measurements of Roessler and Faxfog (ref.22) and Szkarlat and Japar (ref.23), who obtain an average value of 8.3 m^2/g at 0.5 μ. For these three examples, the optical depths due to absorption are respectively 0.052, 0.033, and 0.023. These optical depths are large enough to produce significant changes in the radiation balance over a highly reflecting surface (refs.14,15). This is illustrated by the calculations of Porch and MacCracken (ref.14) and of Cess (ref.15), who have modeled the Arctic aerosol for an absorption optical depth of 0.021 (which is close to our minimum estimate), cloud-free conditions,

a zenith angle of 72°, and a surface albedo of 0.8. For these parameters, they obtain a change in the noontime solar radiation balance at the top of the troposphere of about 20 W/m^2. When averaged over the day for March 15 at 70° N, the surface-atmosphere energy absorption would increase by about 7 W/m^2 (refs.14,15). These changes are substantial and would correspond to an increase in the energy absorbed by the earth-atmosphere system of approximately 5% of the incident solar flux at the top of the troposphere. Correspondingly larger changes would be expected for the internally mixed aerosol models. These first estimates of the effects of graphitic carbon on the Arctic radiation balance are based on the flight profile shown in Fig. 3, which is obviously only over a small geographical region and in a narrow time frame. Similar vertical profiles in other areas of the Arctic will be available in the future.

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REFERENCES

1 G.W. Paltridge and C.M.R. Platt, Radiative Processes in Meteorology and Climatology, Elsevier, Oxford, 1976.
2 H. Rosen, A.D.A. Hansen, R.L. Dod and T. Novakov, Science, 208 (1980) 741-743.
3 H. Rosen, A.D.A. Hansen, L. Gundel and T. Novakov, Appl. Opt., 17 (1978) 3859-3861.
4 C.I. Lin, M. Baker and R.J. Charlson, Appl. Opt., 13 (1973) 1356-1363.
5 K.A. Rahn and R.J. McCaffrey, Ann. N.Y. Acad. Sci., 338 (1980) 486-503.
6 G.E. Shaw, Atmos. Environ., 15 (1981) 1483-1489.
7 H. Rosen, T. Novakov and B.A. Bodhaine, Atmos. Environ., 15 (1981) 1371-1374.
8 L.A. Barrie, R.M. Hoff and S.M. Duggupaty, Atmos. Environ., 15 (1981) 1407-1419.
9 B. Ottar, Atmos. Environ., 15 (1981) 1439-1445.
10 J. Heintzenberg, Tellus, 32 (1980) 251-260.
11 B.A. Bodhaine, T.M. Harris and G.A. Herbert, Atmos. Environ., 15 (1980) 1375-1389.
12 J.M. Mitchell, Jr., J. Atmos. Terr. Phys., Special Suppl. (1957) 195-211.
13 G.E. Shaw and K. Stamnes, Ann. N.Y. Acad. Sci., 338 (1980) 533-539.
14 W.M. Porch and M.C. MacCracken, Atmos. Environ., 16 (1981) 1365-1371.
15 R.D. Cess, Atmos. Environ., accepted for publication (1983).
16 F. Tuinstra and J.L. Koenig, J. Chem. Phys., 53 (1970) 1126-1130.
17 G.T. Wolff and R.L. Klimisch, eds., Particulate Carbon: Atmospheric Life Cycle, Plenum, New York, 1982.
18 A.D.A. Hansen, H. Rosen and T. Novakov, Appl. Opt., 21 (1982) 3060-3062.
19 T.P. Ackerman and O.B. Toon, Appl. Opt., 20 (1981) 3661-3668.
20 P. Chylek, V. Ramaswamy, R. Cheng and R.G. Pinnick, Appl. Opt., 20 (1981)

2980-2985.
21 K.T. Whitby, Atmos. Environ., 12 (1978) 135-141.
22 D.M. Roessler and F.R. Faxfog, Appl. Opt., 69 (1979) 1699-1704.
23 A.C. Szkarlat and S.M. Japar, Appl. Opt., 20 (1981) 1151-1155.

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